ENERGY

DOE/PC-700

CHEMICAL PRODUCTION FROM
WASTE CARBON MONOXIDE—ITS POTENTIAL FOR
ENERGY CONSERVATION

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Date Published—November 1977

Prepared for the Department of Energy (DOE)
Office of Conservation
Division of Industrial Energy Conservation
Contract No.: EY-76-C-06-1830

Energy and Waste Technology Section
Chemical Technology Department

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Pacific Northwest Laboratories
Richland, Washington 99352

U. S. DEPARTMENT OF ENERGY

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.50
026-050	\$5.00
051-075	\$5.50
076-100	\$6.00
101-125	\$6.50
126-150	\$7.00
151-175	\$7.75
176-200	\$8.50
201-225	\$8.75
226-250	\$9.00
251-275	\$10.00
276-300	\$10.25

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FOREWORD

This report summarizes the results to date of a study to determine the potential for energy conservation by utilizing by-product or waste carbon monoxide from industrial sources as a chemical feedstock. This study is being performed by Battelle-Northwest for the DOE Division of Industrial Energy Conservation under the direction of Dr. Jermome F. Collins, DOE Project Manager, whose assistance and helpful direction is gratefully acknowledged.

A special acknowledgement is given here to John Varga, Jr. of Battelle Memorial Institute, Columbus Laboratories, who provided most of the data on the iron and steel industry. The authors also wish to thank the many representatives of industry who contributed valuable information for this report. Special thanks go to:

- Dr. Robert Allenbach, Union Carbide Corporation, Niagara Falls, NY, ferroalloys.
- Mr. Richard Bartoo, The Benfield Corporation, Pittsburgh, PA, carbon dioxide removal.
- Mr. Norman Bliss, Alabama Alloys, Inc., Birmingham, AL, ferroalloys.
- Mr. Vincent Cherene, Kaiser Steel Corp., Oakland, CA, iron and steel.
- Mr. Del Dow, Kaiser Aluminum Corp., Permanente, CA, aluminum.
- Mr. R. A. Griffin, Kerr-McGee Chemical Corp., Hamilton, MS, titanium dioxide.
- Mr. Lewis Haish, Aluminum Company of America, Vancouver, WA, aluminum.
- Mr. Robert Harvard, Cities Service Company, Monroe, LA, carbon black.
- Mr. William Hillman, E. I. DuPont de Nemours and Company, Inc., Antioch, CA, titanium dioxide.
- Mr. Donald E. Lackner, The Carborundum Company, Vancouver, WA, silicon carbide.
- Mr. T. Lopuszynski, Union Carbide Corp., Ashtabula, OH, calcium carbide and ferroalloys.

- Mr. James Ord, The New Jersey Zinc Co., Palmerton, PA, zinc.
- Mr. O. J. Quartulli, Pullman-Kellogg Division of Pullman, Inc., Hackensack, NJ, ammonia plants.
- Dr. D. J. Robinson, Cabot Corporation, Pampa, TX, carbon black.
- Mr. Donald Ryan, Anaconda Aluminium Company, Columbia Falls, MT, aluminum.
- Mr. A. Seeds, Charcoal Briquette Institute, Oakbrook, IL, charcoal.
- Mr. Alexander Thompson, Martin-Marietta Corp., Goldendale, WA, aluminum.
- Mr. R. Wintersteen, Airco Inc., Niagara Falls, NY, ferroalloys, and many others.

EXECUTIVE SUMMARY

This report summarizes the results to date of an ERDA Office of Conservation Study of the potential for energy conservation by producing chemicals from by-product or waste carbon monoxide (CO) from industrial sources. Extensive compilations of both industrial sources and uses for carbon monoxide were developed and included. Reviews of carbon monoxide purification and concentration technology and preliminary economic evaluations of carbon monoxide concentration, pipeline transportation and utilization of CO in the synthesis of ammonia and methanol are also included.

Major U.S. industrial sources of CO were identified: iron, steel and coke; ferroalloys; carbon black; calcium carbide; aluminum; phosphorus, plus many smaller sources. Much of this by-product CO is used as fuel, particularly in the iron and steel and phosphorus industries. However, of the estimated 140 million tons/yr of CO produced by industry as a by-product gas, 85 million tons are recoverable. Of the recoverable portion, 63 million tons are used as fuel and 21 million tons are wastefully flared. A substantial portion of the 63 million tons used as fuel could probably be replaced by coal. Discussions with phosphorus industry representatives indicated that most of the CO used for fuel in that industry could easily be replaced by coal. Some plants already use coal when by-product CO is unavailable.

Large volumes of CO are generated by the chemical industry for use as a chemical intermediate in making methanol, ammonia, urea, isocyanates and other major chemicals. Nearly all of this CO is derived via natural gas reforming. In several cases, chemical plants are generating CO from natural gas while other plants nearby are flaring their waste CO. The production of major chemicals such as methanol, ammonia, acetic acid, acetic anhydride, urea, isocyanates, acrylonitrile, and higher alcohols which use carbon monoxide was summarized. Potential future requirements for CO in developing chemical routes to major chemicals were identified. They include the direct synthesis of isocyanates from nitro-compounds, and direct syntheses of adipic acid and maleic anhydride from acetylene and CO, as well as many other possible products.

Most industrial by-product CO is impure and often dilute (less than 20% CO), so it must be concentrated and purified before it can be used for chemical synthesis. The options commercially available for CO concentration and purification have been compared, and many possible future options identified. With natural gas prices expected to increase, and its availability to decrease, CO will become more attractive as a replacement for natural gas. However, advances in CO concentration and purification technology are needed such that the costs of CO concentration will be reduced significantly.

The cost of concentration and purification of gray iron casting cupola off-gas containing 15% CO, using the COSORB process, is about $\$0.98/10^3$ SCF of CO. This assumes no value for the crude feed material. Another study indicates about $\$0.48/10^3$ SCF of CO for COSORB processing of similar gas at a much larger scale.

The economics of transporting industrial by-product CO were studied. Generally, it is more economical to shift CO to hydrogen (assuming H₂ is desired) and transport the hydrogen by pipeline to its place of use, than to transport CO to its point of use and then form hydrogen.

Preliminary technical and economic feasibility studies were made of producing ammonia and methanol from the by-product CO produced by a typical elemental phosphorus plant. Methanol synthesis appears to be more attractive than ammonia synthesis when using CO feedstock because of reduced water gas shift and carbon dioxide removal requirements.

The economic studies indicate that methanol synthesis from CO appears to be competitive with conventional technology when the price of natural gas exceeds \$0.82/million Btu, while ammonia synthesis from CO is probably not competitive until the price of natural gas exceeds \$1.90/million Btu. The above evaluations probably represent the most optimistic case for chemical synthesis from by-product CO since the off-gas from an elemental phosphorus plant is about 98% CO and does not require concentration. However, the production costs of both chemical commodities appear to be competitive in today's market place if CO is available at zero cost. Even when concentration and

purification of CO is required prior to ammonia or methanol synthesis, the production costs can be expected to become competitive in the next five years as the chemical industry shifts to more expensive processing of heavy petroleum feedstocks.

Economic estimates made in this study indicate that the requirement for preconcentration of CO via the COSORB process increases the production in cost of methanol by 35-70%.

This report also includes an extensive bibliography listing of the available literature on CO production, recovery and use.

There appears to be considerable potential for energy conservation in the chemical industry, by collecting CO rather than flaring it, and using it to make major chemicals such as ammonia and methanol. This potential will be more critically explored in further phases of this work.

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CONCLUSIONS

1. The quantities of CO released from industrial processes are very large but cover a great variety of processes in dispersed locations. The total annual amounts from major sources are estimated to exceed 140,000,000 tons (1.2×10^{15} Btu).
2. Where concentrations of the vented gas are high enough the gas is most generally used as a fuel. Much dilute gas is flared or otherwise discharged with a minimum of treatment. Such unutilized gas is estimated to exceed 20,000,000 tons (1.7×10^{14} Btu) per year in the U.S. Much of this gas, as well as that used as fuel, may be applied to higher valued uses such as chemical production.
3. Many major chemical products require the production and conversion of CO as a major raw material. Essentially all of this CO is derived from natural gas (methane) for products such as ammonia and methanol, and their important primary derivatives such as urea, formaldehyde and acetic acid.
4. With anticipated further future escalation of natural gas (methane) prices and inadequate supplies in some regions, certain existing processes needed to separate, purify and concentrate CO will be justified in a number of situations. This will certainly be the case when natural gas prices of about \$3/million Btu are achieved. Already, in local areas, prices have risen precipitously in a very short time to about \$2/million Btu.

5. There are significant uncertainties as to the actual quality and composition of waste CO with regard to its suitability for conventional chemical production involving sensitive catalytic processes such as ammonia and methanol production. However, there appear to be favorable prospects via conventional processes for the adequate removal of anticipated contaminants such as carbon dioxide, sulfur, phosphorus and fluorine compounds, as well as particulate matter.
6. In view of anticipated shortages and higher prices for natural gas the recovery and more productive use of even a fraction of the total available waste CO would result in significant conservation results via natural gas displacement. For example, 4.3×10^{13} Btu of natural gas could be saved if just 25% of only the presently unutilized gas were recovered.
7. Because of its relatively low heat value compared with hydrogen or methane as well as its much greater density, CO is not likely to be economical for delivery by pipeline over appreciable distances. Therefore, its use will most likely be confined to onsite or closely neighboring facilities.
8. Where geographic marketing factors are favorable, the most likely uses for CO will be the manufacture of methanol, methanol derivatives such as formaldehyde and acetic acid, and ammonia. There may be individual cases where special conditions are favorable for other major products such as phosgene and vinyl acetate.
9. Waste CO is recoverable via two different processes from two classes of industries: a) those producing the gas in high concentrations or rich gases in which the only major diluent is carbon dioxide for which a simple scrubbing process would suffice; and b) those producing gas which is highly diluted, principally with nitrogen, for which more elaborate extraction processes would be needed such as cryogenic, copper-ammonium solvent or COSORB.
10. The preferred order for considering CO recovery from those industries venting concentrated gas would be: a) elemental phosphorus, b) electrothermic zinc reduction; and c) ferroalloy and calcium carbide production utilizing sealed or semi-sealed furnaces.

11. The preferred order for considering carbon monoxide recovery from those industries venting gas with intermediate CO concentrations would be:
 - a) suppressed combustion basic oxygen steel furnaces (BOFs) and, b) grey iron casting cupola furnaces.
12. The preferred order for considering carbon monoxide recovery from those industries venting dilute gas would be: a) iron blast furnace gas, b) petroleum refinery cracking-catalyst regeneration gas, and c) carbon black production.
13. Refinements to the data presented in this report are expected to be made through continued efforts on this study.
14. The problems which need to be resolved or critically analyzed in order to enhance the promotion of a practical application of the results of this study include the following:
 - a) Representative and rather complete analyses of the composition of likely gases from the industries listed above.
 - b) Identification of gas quality requirements for the major proposed uses of recovered CO.
 - c) Determine the engineering and process requirements for a feasible gas collection, delivery and/or accumulation system for a few most likely industrial sources of CO.
 - d) Provide detailed economic studies in support of the various process and product alternatives.
 - e) Development of a pilot or demonstration plant program for a specific industry and product by cooperative arrangement between industry, ERDA and the research organization.

RECOMMENDATIONS

In view of the encouraging energy conservation possibilities as well as apparent production opportunities which this study indicates, the following actions are recommended for the next phase of the study to promote the realization of the probable and practical benefits:

1. Through cooperation with participating industries, obtain confirmation of the availability, quantities, quality of by-product CO including accurate and representative particulate and chemical analyses for gross as well as critical minor components contained in the gas streams, and practical ranges for these.
2. Conduct laboratory investigations of proposed means for gas clean-up and purification as required for the intended production applications.
3. Complete detailed engineering and refined economic studies for specific cases of CO recovery, purification and conversion to hydrogen, methanol and/or ammonia. These studies should include a comprehensive unification of material costs, processing costs and future values.
4. For those industries which appear to have the most favorable prospects for CO recovery and use, conduct an investigation for the likely practical means by which CO production or quality may be improved to provide justifiable benefits.
5. Obtain agreements from representative industries or plants to cooperate and/or participate in continuation of specific features of this study leading to a shared-cost pilot or demonstration project(s).

INTRODUCTION

Carbon monoxide is a substance which has been a recognized entity for thousands of years because of its toxicity. It gained notoriety as the "after damp" in mines--a lethal gas from the incomplete combustion of methane ("fire damp") during mine gas explosions.

As a chemical, its history is much shorter. An evaluation of the uses of natural gas and petroleum for petrochemical manufacture reveals that CO is an intermediate in many petrochemical processes. In fact, CO may be substituted for natural gas in most instances.

Natural gas is still wastefully flared in some parts of the world in order to expedite petroleum recovery, but in the United States it is rapidly becoming a precious commodity. The recent shortages in supply and price escalations for natural gas are expected to continue with increasing severity in the future. In anticipation of this, major efforts are underway to find alternative sources of natural gas and to develop synthetic substitutes. Since much of the natural gas used chemically is converted to CO and hydrogen via steam reforming, the possibility of producing CO from other sources warrants serious attention.

An obvious way to produce CO is by gasification of coal,⁽¹⁾ since coal is plentiful. Before the advent of natural gas, coal was widely gasified for domestic and industrial use. However those techniques do not meet modern needs in terms of efficiency or economics⁽¹⁾ and there are about a dozen new processes being developed for coal gasification.

Other ways have been proposed for making CO in a reasonably pure state: reaction of carbon dioxide with carbon;^(2,3) reaction of sulfur dioxide with coal-derived char;⁽⁴⁾ from municipal trash;^(5,6) from sewage;⁽⁷⁾ from carbonaceous waste-derived coke, carbon, or char;⁽⁸⁾ or even from the reduction of carbon dioxide with hydrogen.⁽⁹⁻¹²⁾ A steam/phosphorus and phosphoric oxide/carbon cycle has been proposed,⁽¹³⁾ as well as other exotic CO production methods.^(14,15)

However, few of these processes are expected to be important in the near future, with the probable exception of CO derived from carbonaceous materials and coal.

The most common method currently used by industry to generate CO is the steam reforming of natural gas or the partial oxidation of hydrocarbon oils. Although a review of the extensive literature on this subject is beyond the scope of this report, some representative examples describing this advanced technology are the conversion of hydrocarbon fuel oils⁽¹⁶⁻²³⁾ and natural gas⁽²⁴⁾ to CO, for use in the blast furnace as a fuel gas,⁽²⁵⁾ or in polyurethane plastics manufacture,⁽²⁶⁻²⁸⁾ or for the production of hydrogen by the water gas shift reaction (e.g., 29,30) or thermochemically.⁽³¹⁾ It has even been suggested that waste heat from nuclear power plants be used to power the hydrocarbon to CO conversion process.^(32,33)

With present technology, the steam reforming of natural gas is an everyday practice and hydrocarbon oil reforming is also performed. Coal gasification is commercially proven but is not used for CO generation in this country. The gasification of carbonaceous wastes is proven on a pilot plant scale, and the other processes listed are speculative or demonstrated in the laboratory only.

This very brief survey of CO production has indicated that it is a bulk chemical. Since it is normally not transported but rather used at the production site by the producer, its scale of production does not show on any list of bulk chemical commodities. A following section indicates the great versatility and scale of use of CO in industry, both for chemicals manufacture and as a fuel.

To discuss the relative importance of man-made and natural sources of CO, and introduce a discussion of conservation in contrast to production, a brief discussion of the pollution problem is necessary. This will be done with reference to a few key documents rather than by attempting a complete survey. Those interested in pollution aspects of CO production are referred to comprehensive summaries of the global distribution,⁽³⁴⁾ spectra,⁽³⁵⁾ emission regulation,^(36,37) measurement and concentration

techniques,⁽³⁸⁻⁴¹⁾ toxicity,⁽⁴²⁻⁴⁵⁾ health hazard in industrial plants in the U.S.,^(46,47) in the USSR,⁽⁴⁸⁻⁵²⁾ and in Iran,⁽⁵³⁾ and to the relation of CO exposure and sickness,⁽⁵⁴⁾ and multiple sclerosis.⁽⁵⁵⁾

The average atmospheric concentration of CO is 0.10 to 0.15 ppm; this is relatively constant, although temporal and spatial fluctuations occur within the range of 0.01 to 0.20 ppm in remote locations, and 0.4 and 2.2 ppm in urban areas.⁽³⁵⁾ A 12% decrease in airborne CO since 1970 has been reported.^(56,57) Carbon monoxide is part of the stratospheric ozone balance, being ultimately oxidized to carbon dioxide by ozone. The major natural sources are volcanic activity, decomposition of living organisms, plant metabolism (including brown algae), and the photolysis of dissolved carbonaceous materials.⁽³⁴⁾ A recent article⁽⁵⁸⁾ dealing with the chemical synthesis of organic molecules on Mars, from ultraviolet irradiation of CO, permits the inference that the synthesis/degradation cycle mediated by long wavelength UV light could be the basis for a global CO cycle on the Earth.

It has been estimated that man-made sources provided about 400 million short tons globally of CO in 1970, 150 million short tons in the U.S., and that natural sources provided 3 to 25 times that.⁽³⁴⁾ The total is broken down in Table 1, showing that industrial waste CO in the U.S. was at least 11 million tons/yr (in 1971), and in fact is certainly much higher, since the compilation included only known sources of record.

Despite the presence of 3 billion people on the Earth, man's share of CO production is only about 4% of the total. In fact, some 3000 short tons/yr arise from the decomposition of human hemoglobin in normal biochemical metabolism.

The problems associated with CO are therefore not a result of global contamination, but rather the concentration of CO sources in localized areas in and around urban centers and industrial plants. By identifying these sources, their concentrations, quantities, methods of collection, and most importantly, ways of achieving their use for conversion into chemical products, the dual functions of energy conservation and a reduction in the inventory of natural gas required by industry may be achieved.

TABLE 1. U.S. Production Sources and Quantities of CO^(a)

<u>Man-Made</u> ^(b)	<u>x 10⁶ Tons</u>
Fuel combustion	0.8
Transportation	110.9
Solid waste disposal	7.2
Industrial off-gases	11.4
Refuse, structures, and agricultural burning	<u>15.9</u>
Total	146.2
<u>Natural</u>	
Volcanoes	
CH ₄ photo-oxidation	
Algae and plankton	
Terpene photochemical oxidation	
Chlorophyll degradation	<u> </u>
Total	440 to 3750

(a) 1970 figures (after Reference 34).

(b) Conservative figures--identified sources only.

DISCUSSION

OBJECTIVES AND SCOPE OF STUDY

The overall objective of this project is to identify means by which significant energy conservation may be achieved, through productive and economical applications for the lost or underused CO in certain industrial waste gases in the U.S.

Many typical reduction processes in metallurgy and mineral processing evolve substantial quantities of CO in process vent gases. Particularly in the iron and steel and elemental phosphorus industries, the concentration and quantity of this by-product gas have been sufficient to encourage its use as a fuel for preheating furnace air, ore drying, and metal processing. In certain other industries, such as the aluminum industry, no productive use of such waste gas is made.

As conventional fuel prices increase, particularly for natural gas and crude oil, waste or by-product CO from a greater variety of industries would be expected to be considered as a fuel in those industries which need this form of energy. As natural gas prices increase it will become more valuable as a chemical feedstock for the production of hydrogen, methanol, ammonia, and/or urea, and derived chemicals.

The possibilities for such beneficial use of CO in industrial waste gases are the chief concern of this study. Typical industries chosen for study were: iron and steel, aluminum, elemental phosphorus, ferroalloys, silicon, carbon black, titanium dioxide and calcium carbide. During the study, we intended to identify such industries nationwide by specific plants and locations; establish the extent to which waste gas is beneficially used in these plants; identify processes by which the quality of the waste gas may be enhanced (concentrated and purified); and identify the likely products which may be most beneficially produced from such by-product CO. Economic studies of most likely beneficial uses are also a part of this study. Other benefits which may result from utilization, such as improved environmental controls and reduced emissions, and the significance of waste-gas utilization to energy conservation were also to be examined.

Some of the industries listed as the major ones to receive attention in this study were dropped early in the period because of lack of significant potential. They were too small, experience present beneficial use, or anticipated difficulties in achieving adequate gas quality. However, during the study other industries were shown to be of interest. The present list shows no specific cases in the area of petroleum or organic chemical-based industries which evolve CO--although such would appear to be likely. In this case, industrial reluctance to discuss the problem was a major roadblock.

The following results were obtained from our research to date:

1. A national inventory of those process industries which evolve large quantities of CO. This list identifies the specific industries, location and ownership of plants, product capacities, CO outputs and quality and present use or disposition.
2. Chemical feedstock uses which appear to be promising for CO and the impact on energy conservation resulting from such uses (crude oil or natural gas conservation).
3. Means by which the gas can be concentrated and suitably purified for further processing.
4. A preliminary economic evaluation of CO compared with methane for specific feedstock uses was determined.

CURRENT PRODUCTION AND DISPOSITION OF CARBON MONOXIDE

There are no figures published for the total tonnage of CO produced annually by U.S. industry, although enormous amounts of this chemical are produced. This is because very little CO is produced by one company, transported, and used by another. Most CO is used captively as part of a process for the manufacture of other materials, such as methanol, acetic acid, or polyurethanes. Typically, either a natural gas steam reformer or a heavy oil partial oxidation unit (more recently) have been coupled directly to a cryogenic separations unit and other purification equipment, and the producer gas so obtained used directly. Thus, although CO has been an industrially important chemical for many years, as an intermediate for chemicals manufacture,⁽⁵⁹⁾ its scale of use is effectively "hidden."

Rising natural gas prices have increased interest in making producer gas from coal. In South Africa, gasoline is produced at the Sasol I plant by the Fischer-Tropsch method, using coal-derived producer gas.⁽⁶⁰⁾ A second unit of three times the capacity of Sasol I is planned.⁽⁶¹⁾ In the U.S., growing requirements for CO in chemical manufacture have caused Du Pont and National Distillers and Chemical Corp. to announce a joint venture for synthesis gas production,⁽⁶²⁻⁶⁵⁾ producing 600,000 tons/yr of methanol (Du Pont) and 100,000 tons/yr of acetic acid (Distillers). Natural gas is expected to be the feedstock for this Houston area plant, which is due to be completed in 1979. Union Carbide is having a synthesis gas production unit constructed at Institute, W. Va.^(66,67) to produce hydrogen (15.4 million scf/d) and CO (2.9 million scf/d), for organic chemical production.

These examples indicate the scale of CO usage in the U.S. To obtain an approximate numerical value of the potential impact carbon monoxide utilization could have on chemical manufacture, it was necessary to work back from published production figures for the major chemicals which could be derived from CO. Exclusive of fuel use, an approximate calculation yielded a figure of not less than 51 million tons/yr of potential CO utilization for chemical production in the U.S. (For a detailed breakdown of this, see Table 2.)

The very large sources of CO waste gas have received little attention as possible sources for chemicals manufacture (Table 3). Waste gas from calcium carbide or aluminum plants has been claimed as a starting material for ammonia synthesis,⁽⁶⁸⁾ and waste blow gases in steelmaking similarly claimed for methanol synthesis.⁽⁶⁹⁾ Power gas has also been suggested for methanol manufacture.⁽⁷⁰⁾ However, because of low natural gas prices there has been little economic incentive to develop this technology. The estimated potential CO requirement for chemicals manufacture in the U.S. is greater than 51 million tons/yr. Estimated CO production as by-product gas is 142 million tons, of which about 63 million tons are used as fuel and 21 million tons are exhausted or flared (Table 4).

TABLE 2. Estimated Potential for Carbon Monoxide Consumption
in Major Industrial Chemical Manufactur

Chemical	Current (a) Production	Potential CO Requirements (a)	Production Route w/CO	Volume Rank Organic Chem- ical Industry	Volume Rank Organic Chemical Market	Volume Rank Rank of Volume all U.S. Chemical Industry
Ammonia, anhydrous	16.5	40.8	via water/gas shift reaction + N ₂	--	--	3
Urea, primary solution	3.9	5.46	via NH ₃ with waste CO ₂	2	9	15
Methanol	3.1	8.2	via H ₂ and CO	3	3	14
Formaldehyde 37%	2.8	2.9	via MeOH, oxide	5	24	22
Acetic Acid	1.2	2.2	via MeOH and CO	12	17	36
Acetic Anhydride	0.8	1.7	via Acetic Acid	19	13	44
Vinyl Acetate	0.7	0.9	via Acetic Acid with Ethylene	28	27	50
Phosgene	0.31	.09	with Cl ₂	35	45	--
Toluene 2, 4 and 2, 6-diisocyanate	0.15	.05	via phosgene with Dinitro- toluenes	58	21	--
Acrylic Acid	0.05	.02	with Acetylene and H ₂ O	79	62	--
Ethyl Acrylate	0.10	.03	with Acetylene and EtOH	63	49	--
n-Butyl Acrylate	0.04	.04 + .01	with Acetylene and n-Butanol	92	69	--
N-Propanol	0.03	.04	with Ethylene	107	96	--
n-Butanol	0.24	.23	with Propylene and H ₂	44	46	--
Isobutyl Alcohol	0.04	.04	with Propylene and H ₂	85	98	--
Isooctyl Alcohols	0.05	.03	with Heptenes and H ₂	80	89	--
2-Ethyl Hexanol	0.23	.15	with Propylene or Heptenes and H ₂	45	47	--
Decyl Alcohols	0.08	.04	with Trimerized Propylene and H ₂	69	73	--
Total		50.94				

(a) millions of short tons/yr

(b) not included in total to eliminate double counting

TABLE 3. Estimated Annual Production^(a) of
By-Product Carbon Monoxide

	<u>Produced Theoretically</u>	<u>Recoverable from Process</u>	<u>Used at Present^(b)</u>	<u>Flared or Exhausted</u>	<u>CO Content, vol%</u>
Iron and Steel					
Sinter	1,090(41)	1,090(41)	0	1,090(41)	0.35
Blast	56,280(53)	56,280(53)	43,898(53)	12,382(53)	22.5
BOF without Sup- pressed Combustion	28,126(36)	527(36)	0	527(36)	0.3
BOF with Suppressed Combustion	3,781(2)	3,781(2)	3,781(2)	0	50
Electric	25,751(125)	294(125)	0	294(125)	0-6
Ferroalloys					
FeMn	976(9)	617(1) na(8)	543(1)	74(1) na(8)	40
FeCr	413(10)	na(10)	0	na(10)	
FeSi	1,484(15)	300(3) na(12)	78(1)	222(3) na(12)	90
SiMn	148(8)	44(1) na(7)	0	44(1) na(7)	65
Other Alloys	250(11)	na	0	na	
Coke Ovens	2,439 ^(a) (63) ^(b)	2,439(63)	2,439(63)	0	6
Silicon Products	370(10)	na	0	na	
Aluminum	1,695(32)	244(5)	0	244(5)	30
Phosphorus	1,316(9)	1,316(9)	1,184(9)	132(9)	98
Titanium Dioxide	275(8)	275(8)	0	275(8)	15
Carbon Black (furnace)	2,275(29)	2,275(29)	33(1)	2,242(29)	6
Calcium Carbide	183(5)	165(3)	65(2)	100(3)	75
Lead and Tin	363(7)	363(7)	0	363(7)	<1
Zinc (thermal)	162(2)	162(2)	142(2)	20(1)	80
Petroleum Refining	14,561(149)	14,561(149)	10,921(112)	3,640(37)	8
Kraft Paper Pulping	160(116)	160(116)	0	160(116)	<1
TOTAL	142,098	84,893	63,084	21,709	

(a) Thousands of tons/yr of CO (number of sites in U.S.)

(b) Used entirely as fuel.

na Negligible CO available for recovery under present process conditions.

TABLE 4. By-Product Carbon Monoxide Sources and Uses

CO Source	Quantity ^(a)	Fate
By-Product	142	--
Not Recoverable	57	(b)
Recoverable	85	--
Recovered	63	Fuel
Not Recovered	22	Flared or Exhausted

^(a) Millions of short tons/yr.

^(b) The remainder is vented as dilute gas or oxidized to CO₂ at the furnace/air interface.

THUS, ALMOST 50% OF THE CO WHICH COULD BE POTENTIALLY USED FOR CHEMICAL SYNTHESIS COULD BE OBTAINED FROM INDUSTRIAL BY-PRODUCT GASES WHICH ARE CURRENTLY FLARED.

It can be seen from the preceding tables that the major industrial requirement for CO could be in the production of ammonia, methanol, and acetic acid and their derivatives. Some 51 million short tons/yr of CO could be consumed in making these chemicals. The iron and steel industry produces by far the greatest amounts of by-product CO (117 million tons/yr), with large amounts also being produced in the petroleum refining (14.5 million tons/yr), ferroalloys (3 million tons/yr), coke, carbon black, phosphorus and aluminum industries (7.7 million tons/yr). Of this total CO production, a significant amount is either flared or exhausted to the atmosphere. The flared CO gas is produced in greatest amounts in blast furnaces (12 million tons/yr), carbon black (2.2 million tons/yr), and petroleum refining operations (3.6 million tons/yr). Further potential for CO recovery exists if the gas currently used as a fuel can be replaced by coal. However, the relative importance of the various individual industries as waste CO producers is complicated by problems such as the numbers of plants producing CO, and their geographical locations in relation to potential users. Thus, it is not possible to compile

a list of CO source priorities for possible waste CO users, as the economics of recovery and use will vary from case to case. It is only possible to say that, based on the information compiled in Tables 2 to 5, 50% OF THE POTENTIAL U.S. CO REQUIREMENT FOR CHEMICALS MANUFACTURE COULD BE SUPPLIED BY CO BY-PRODUCT GAS WHICH IS CURRENTLY BEING FLARED. This figure could be increased even more if allowances are made for replacement of CO currently used as a fuel by coal, or new technology for gas collection applied to some industries.

INDUSTRIES GENERATING CARBON MONOXIDE-BEARING WASTE GAS

This section identifies U.S. industries which generate by-product CO. Carbon monoxide is generated in two major ways: reduction of ores to elements or simpler compounds, in which oxygen is abstracted by carbon to form CO; or through incomplete oxidation of carbon. Examples of oxygen abstraction by carbon are the reduction of metal ores to iron, lead, etc., the production of elemental phosphorus by reduction of phosphates, the reductive chlorination of rutile in making titanium dioxide, and the production of calcium and silicon carbides.

Alternatively, CO is generated through incomplete oxidation of carbon, either at the carbon anodes of electrolytic cells or in the generation of carbon black by incomplete oxidation of hydrocarbon oils:

The quality of the CO generated varies with the process. In elemental phosphorus production the off-gases are up to 98% CO, while in silicon carbide production, the off-gases contain less than 1% CO. The reason for the difference is the furnace configuration: in phosphorus production, the off-gases are collected and do not come into contact with air, while in silicon carbide manufacture, virtually all of the CO burns at the surface of the furnace where it comes into contact with air. Other processes use partial burning with air so that the resulting CO contains nitrogen as a diluent. Individual processes may also have specific diluents peculiar to the process, usually carbon dioxide or contaminants, such as phosphorus, hydrogen fluoride, or hydrogen sulfide.

IRON, STEEL, AND COKE

Production of steel is the primary U.S. industry which also generates large quantities of CO. Iron oxide ores such as limonite, hematite, and magnetite are heated in a blast furnace with flux and coke. The coke is derived from coal pyrolysis, which itself generates CO. However, since most of the coking industry is captive to the iron and steel industry, it is treated together with iron and steel. Iron, steel and coke production sites in the U.S. are shown in Figure 1.

Nowadays blast furnace gas is used as a fuel for the process, following many years of development of systems by which the blast furnace off-gas can be trapped and recycled⁽⁷¹⁻⁷⁴⁾ or converted to synthesis gas.⁽⁷⁵⁾ Originally, this gas was simply flared, although today even with gas recycling there are difficult pollution problems.⁽⁷⁶⁻⁷⁹⁾ Without recycling, the iron and steel industry would be in serious trouble. The use of recycled blast furnace gas requires less coke and results in economies, although purification steps⁽⁸⁰⁾ for dust removal, or in one case conversion to hydrogen⁽⁸¹⁾ tend to offset the economy somewhat. The injection of gaseous reductants into a blast furnace requires sophisticated measurement and control equipment.^(82,83) The large volume of literature on iron/CO and hydrogen reduction kinetic and equilibrium studies (e.g., 84-92), indicates the continuing development in iron production technology.

Recent trends in iron production have been towards injecting hydrocarbons as a reducing material to supplement the coke. The hydrocarbons range from heavy fuel oil to natural gas.⁽⁹³⁻⁹⁵⁾ In some cases, steam reformed natural gas (producer gas) is used.⁽⁹⁶⁾ With increased gas and oil prices in the U.S. this process is not expected to be used much in the future, although in countries with a surplus of petroleum it may gain ground.⁽⁹⁷⁻⁹⁹⁾

The current method of iron production in a blast furnace has been used for many years, and is unlikely to be modified substantially in the foreseeable future. Although the potential use of non-oxide ores in ironmaking does exist⁽¹⁰⁰⁾ there is little prospect that these will be needed. In Third World countries, however, direct processes for reducing iron ore without blast furnaces are becoming increasingly important as a small scale method. The direct reduction of iron ore represents a potential use of carbon monoxide.

FIGURE 1. Sites of Steel Production in the U.S.

Conversion of pig iron to steel is done in an open hearth furnace, basic oxygen converter (BOF) furnace, or electric furnace. The BOF process is currently replacing the older open hearth furnace, while electrothermal refining is used more for specialty steels and smaller operations.

Recovery of CO from the off-gases of BOF furnaces has been the subject of extensive patent activity,⁽¹⁰¹⁻¹²⁸⁾ as well as literature articles.⁽¹²⁹⁻¹³⁵⁾ In addition, there have been a number of studies on the kinetics⁽¹³⁶⁻¹⁴⁸⁾ of CO formation in iron and steel production, measurement and analysis techniques for off-gases,^(149,150,122) and specialized uses for the CO-containing off-gas, such as stirring the liquid metal.⁽¹⁵¹⁾ The role of CO in steelmaking has been briefly reviewed.^(152, 153) Since computerized control of the process is now commercially practical⁽¹⁵⁴⁾ and will be more widely used in the future, much more accurate data on off-gas composition and quantity in the BOF process should become available.

Much less work has been done on scrap iron cupola emissions, although one detailed study exists.⁽¹⁵⁵⁾ The magnitude of the off-gas waste problem from this process is illustrated by one Russian report,⁽¹⁵⁶⁾ where a 16 ton cupola yielded 16,000 m³/hr of off-gas, which after dilution with 32,000 m³/hr of natural gas contained 6-21% of CO. This was burned in air to 0.2-0.6% CO, and then discharged to the atmosphere. Unfortunately, little information is available on U.S. emissions from this and similar processes, except as listed later in this section. However, the example given does illustrate the waste of using natural gas to bring a waste CO stream to the correct combustible concentration for conversion to carbon dioxide and subsequent venting to atmosphere, without using any of the chemical or fuel values of the gas.

Electric arc steelmaking furnaces are also sources of waste CO,^(157,158) although the use of the CO generated from the charge and the electrodes to supplement the heating effect of the electric current is now being considered.^(158,159)

In contrast to off-gas recovery from BOF furnaces, the use of off-gases from coke ovens has a long history. A patent issued in 1884 deals with the use of coke-oven gas as a supplemental fuel for heating the oven,⁽¹⁶⁰⁾ and an 1891 patent recommends the collection of CO_2 from coke ovens heating this with carbon to generate CO, and using the CO as a fuel.⁽¹⁶¹⁾ The use of recycled coke-oven gas as a fuel was patented again in 1974,⁽¹⁶²⁾ and the use of off-gas CO as a chemical to convert metals in petroleum coke into volatile carbonyls was recommended as a means of purifying coke.⁽¹⁶³⁾ Recently, the Peabody continuous coking process was developed, where off-gases are used for steam generation or drying.⁽¹⁶⁴⁾ This process is claimed to use all of the off-gas for fuel, and to be virtually pollution free. There would thus be no waste CO available for use.

Current data for the various U.S. iron and steel industry subprocess plants are presented in Tables 5 through 10. The various plants and locations are given in groups conforming to the American Iron and Steel Institute steelmaking districts, as illustrated in Figure 2. Whenever possible, the gas volumes are given for individual plants. However, this was not possible for blast furnaces. Therefore, blast-furnace data are given for geographical groupings of blast furnaces.

Capacities and gas generation are based on 1973 data; that year had the highest production of steel in recent years, and indicates the maximum production capability of the industry.

The by-product coke plants are essentially the refining points for fuel and reductant for the iron and steel industry. Coal is charged to the coke ovens and the two major products are coke and coke-oven gas.

By-Product Coke Plants

Included in Table 5 are coke plants in the integrated iron and steel industry and the merchant coke manufacturers. Merchant coke manufacturers produce coke for the steelmaking industry and for use in ferrous foundries. The estimated coke-oven gas generated by the steel industry (total of Table 5 minus merchant coke producers) is 934,144 million ft^3/yr . In 1973 the

TABLE 5. By-Product Coke Plants and
Estimated Coke-Oven Gas Production

AISI Steelmaking District, Company and Location	Batteries Number	Ovens Number	Coal Used net tons	Coke-Oven Gas Made Million Cubic Feet	Under- firing Percent
<u>Northeast</u>					
Alan Wood Steel Company Swedeland, PA	2	110	667,000	7,050	45.0
Bethlehem Steel Corporation Bethlehem, PA	6	374	2,464,000	26,118	30.0
Sparrows Point, MD	12	747	5,405,000	56,752	0.0
Eastern Gas & Fuel Associates Philadelphia, PA	1	74	698,000	7,378	45.0
United States Steel Corporation Fairless, PA	2	174	2,000,000	20,400	36.0
<u>Pittsburgh</u>					
Bethlehem Steel Corporation Johnstown, PA	4	316	2,435,000	24,350	45.0
Crucible Steel Company Midland, PA	3	113	620,000	6,820	32.0
Jones & Laughlin Steel Corporation Aliquippa, PA	4	327	4,140,000	41,800	40.0
Pittsburgh, PA	4	315	2,900,000	29,435	40.0
United States Steel Corporation Clairton, PA	20	1,375	7,100,000	73,130	45.0
Shenango, Incorporated Neville Island, PA	3	105	943,000	9,967	45.0
Wheeling-Pittsburgh Steel Corporation Monesson, PA	3	93	825,000	8,415	45.0
National Steel Corporation Weirton, WV	3	193	2,412,000	28,944	21.3
Sharon Steel Corporation Fairmont, WV	1	60	338,000	3,465	45.0
Wheeling-Pittsburgh Steel Corporation Follansbee, WV	5	277	2,925,000	3,128	45.0
<u>Buffalo</u>					
Allied Chemical Corporation Erie, PA	1	57	512,000	5,416	45.0
Tonawanda, NY	1	60	539,000	5,696	45.0
Bethlehem Steel Corporation Lackawanna, NY	5	380	3,303,000	32,698	33.0
Donner-Hanna Coke Corporation Buffalo, NY	3	136	1,223,000	12,930	45.0
<u>Cleveland</u>					
Erie Coke & Chemical Company Painesville, OH	2	46	385,700	4,077	45.0
Republic Steel Corporation Cleveland, OH	6	354	2,450,000	24,500	0.0
United States Steel Corporation Lorain, OH	7	224	1,700,000	14,597	43.0

TABLE 5. (Cont'd)

AISI Steelmaking District, Company and Location	Batteries Number	Ovens Number	Coal Used net tons	Coke-Oven Gas Made Million Cubic Feet	Under- firing Percent
<u>Youngstown</u>					
Republic Steel Corporation					
Massillon, OH	1	31	272,000	2,856	36.0
Warren, OH	2	80	715,000	7,508	36.0
Youngstown, OH	3	162	1,670,000	17,368	36.0
Youngstown Sheet & Tube Company					
Campbell, OH	5	380	1,700,000	17,680	36.0
Youngstown, OH	1	84	536,000	5,574	36.0
<u>Cincinnati</u>					
Allied Chemical Company					
Ashland, KY	2	146	1,272,000	13,444	45.0
Ironton, OH	3	168	1,463,000	15,463	45.0
Armco Steel Corporation					
Hamilton, OH	4	110	915,000	9,562	40.0
Middletown, OH	1	76	718,000	7,754	40.0
Cyclops Corporation					
Portsmouth, OH	1	70	600,000	5,820	44.0
Citizens Gas & Coke Utility					
Indianapolis, IN	4	168	1,463,000	15,463	45.0
<u>Detroit</u>					
Allied Chemical Corporation					
Detroit, MI	1	70	832,000	8,795	45.0
Ford Motor Company, Steel Division					
Dearborn, MI	6	250	2,027,000	18,851	0.0
National Steel Corporation					
Ecorse, MI	3	233	2,693,000	28,007	0.0
Interlake, Incorporated					
Toledo, OH	1	57	512,000	5,412	45.0
<u>Southern</u>					
Chattanooga Coke & Chemicals					
Alton Park, TN	2	44	396,000	4,186	45.0
Alabama By-Products Corporation					
Tarrant, AL	6	206	2,111,000	22,318	45.0
Empire Coke Company					
Holt, AL	2	60	147,000	1,554	45.0
Koppers Company					
Woodward, AL	5	256	2,230,000	23,572	45.0
Republic Steel Corporation					
Birmingham, AL	1	65	433,000	4,460	40.0
Gadsden, AL	2	130	870,000	8,961	44.7
U.S. Pipe and Foundry Company					
Birmingham, AL	4	240	2,110,000	22,307	45.0
United States Steel Corporation					
Fairfield, AL	7	489	2,600,000	26,780	36.0
Armco Steel Corporation					
Houston, TX	2	62	765,000	7,650	40.0
Lone Star Steel Company					
Daingerfield, TX	1	78	438,000	4,650	46.0

TABLE 5. (Cont'd)

AISI Steelmaking District, Company and Location	Batteries Number	Ovens Number	Coal Used net tons	Coke-Oven Gas Made Million Cubic Feet	Under- firing Percent
<u>Chicago</u>					
Bethlehem Steel Corporation Burns Harbor, IN	2	164	3,302,000	32,688	35.0
Inland Steel Company East Chicago, IN	8	574	3,850,000	40,810	33.0
United States Steel Corporation Gary, IN	10	746	6,286,000	64,117	36.0
Youngstown Sheet & Tube Company East Chicago, IN	3	237	2,300,000	25,300	44.0
Interlake, Incorporated South Chicago, IL	2	100	920,000	10,120	0.0
Republic Steel Corporation South Chicago, IL	1	75	650,000	6,825	0.0
Wisconsin Steel Division, I-H Co. Chicago, IL	3	166	930,000	9,765	36.0
Koppers Company St. Paul, MN	1	65	562,000	5,941	45.0
United States Steel Corporation Duluth, MN	2	115	785,000	8,086	36.0
Milwaukee Solvay Coke Milwaukee, WI	1	100	328,000	3,467	45.0
<u>St. Louis</u>					
Great Lakes Carbon Corporation St. Louis, MO	3	93	810,000	6,562	45.0
Indiana Gas & Chemical Corporation Terra Haute, IN	2	60	518,000	5,476	45.0
National Steel Corporation Granite City, IL	3	137	1,190,000	12,495	49.0
<u>Western</u>					
CF & I Steel Corporation Pueblo, CO	3	170	1,570,000	17,270	45.0
Kaiser Steel Corporation Fontana, CA	7	315	2,000,000	22,600	0.0
United States Steel Corporation Geneva, UT	4	252	1,730,000	19,030	25.0

FIGURE 2. Steelmaking Districts in the United States

industry consumed 971,655 million ft^3 of coke-oven gas as reported by the American Iron and Steel Institute.⁽¹⁶⁵⁾ This apparent discrepancy is explained by the fact that the coke-oven gas volumes listed in Table 5 are based on heat contents varying from 500 to 600 Btu/ ft^3 of coke-oven gas. AISI statistics are reported on the basis of 500 Btu/ ft^3 of coke-oven gas. Typical compositions of coke-oven gas are given in Table 6.

TABLE 6. Typical Compositions of Coke-Oven Gas

Heating Value Btu per cu ft	Constituents, volume percent					
	CO	CO ₂	H ₂	CH ₄	O ₂	Illuminants
525	5.5	2.2	56.8	28.0	0.0	2.5
530	8.2	2.2	56.2	29.8	0.8	2.2
540	7.3	1.9	56.3	27.8	0.0	3.4
550	4.8	1.6	55.0	28.8	0.6	3.6
575	6.3	2.2	46.5	32.1	0.8	4.0

The major use for coke-oven gas is underfiring (heating) the coke ovens. The percent used for underfiring at each plant is given in Table 5. Excess coke-oven gas is injected into blast furnaces (to conserve coke), used in open hearth furnaces, heating furnaces, annealing furnaces, and has other uses around a steel plant. Essentially none of the coke-oven gas is flared or exhausted.

One of the major problems in using coke-oven gas as a fuel is the sulfur contained in the gas as hydrogen sulfide. Each 1% of sulfur contained in a net ton of coal produces about 400 grains of hydrogen sulfide in each ft³ of coke-oven gas. Desulfurization facilities operate at 83 to 95% efficiency depending on the process used, but not all coke plants are equipped with desulfurization facilities.

Sinter Plants

The sinter process allows for reuse of fines and dust which are lost from the blast furnace. These particles are separated from the blast furnace off-gas, are sintered into large pieces, and are returned to the blast furnace to be changed into iron.

The estimated production of off-gas from sinter plants in the U.S. is given in Table 7 for the individual plants. The off-gas has a very low CO content, as shown by the data in Table 8 reported in a recent study by the U.S. Environmental Protection Agency.

Blast Furnaces

Iron ore, coke and flux are charged to the blast furnace and pig iron is formed. The off-gas produced contains a substantial amount of CO.

The estimated volume of blast-furnace gas produced annually is given in Table 9. It was not possible to estimate the off-gas volume for each blast furnace; the data given are estimates for geographical locations within the various AISI steelmaking districts. Typical compositions of blast-furnace gas are given in Table 10. The composition of blast-furnace gas is influenced by the amount of coke used to produce one ton of pig iron, the carbonate constituents of the materials charged to the blast furnace, the amount of air

TABLE 7. Reclamation (Sinter) Plants and
Estimated Off-Gas Production

AISI Steelmaking District, Company and Location	Estimated Annual <u>Sinter Capacity</u> net tons	Estimated Annual <u>Off-Gas Production</u> million cubic feet
<u>Northeast</u>		
Alan Wood Steel Company, Swedeland, Pennsylvania	500,000	68,000
Bethlehem Steel Corporation, Bethlehem, Pennsylvania	2,400,000	347,000
Sparrows Point, Maryland	4,300,000	540,000
Jones & Laughlin Steel Corporation, Star Lake, New York	1,400,000	145,000
United States Steel Corporation, Fairless, Pennsylvania	3,000,000	334,000
<u>Pittsburgh</u>		
Bethlehem Steel Corporation, Johnstown, Pennsylvania	1,100,000	192,000
Jones & Laughlin Steel Corporation, Alquippa, Pennsylvania	2,700,000	316,000
Unites States Steel Corporation, Braddock, Pennsylvania	600,000	79,000
McKeesport, Pennsylvania	325,000	45,000
Rankin, Pennsylvania	600,000	79,000
Saxonburg, Pennsylvania	4,500,000	667,000
Wheeling-Pittsburgh Steel Corporation, Monesson, Pennsylvania	500,000	77,000
East Steubenville, West Virginia	550,000	72,000
National Steel Corporation, Weirton, West Virginia	2,800,000	255,000
<u>Buffalo</u>		
Bethlehem Steel Corporation, Lackawanna, New York	1,100,000	135,000
<u>Cleveland</u>		
Jones & Laughlin Steel Corporation, Cleveland, Ohio	900,000	203,000
Republic Steel Corporation, Cleveland, Ohio	400,000	54,000
Unites States Steel Corporation, Lorain, Ohio	500,000	68,000

TABLE 7. (contd)

AISI Steelmaking District, Company and Location	Estimated Annual Sinter Capacity net tons	Estimated Annual Off-Gas Production million cubic feet
<u>Youngstown</u>		
Republic Steel Corporation, Youngstown, Ohio	500,000	49,000
Warren, Ohio	400,000	54,000
United States Steel Corporation, Youngstown, Ohio	1,500,000	203,000
Youngstown Sheet & Tube Corporation, Campbell, Ohio	800,000	159,000
<u>Cincinnati</u>		
Armco Steel Corporation, Middletown, Ohio	900,000	159,000
Ashland, Kentucky	800,000	90,000
<u>Detroit</u>		
National Steel Corporation, Ecorse, Michigan	2,000,000	310,000
<u>Southern</u>		
Armco Steel Corporation, Houston, Texas	500,000	63,000
Lone Star Steel Company, Lone Star, Texas	300,000	41,000
Republic Steel Corporation, Gadsden, Alabama	500,000	63,000
United States Steel Corporation, Fairfield, Alabama	2,500,000	320,000
<u>St. Louis</u>		
National Steel Corporation, Granite City, Illinois	1,000,000	126,000
<u>Western</u>		
C F & I Corporation, Pueblo, Colorado	900,000	162,000
Kaiser Steel Corporation, Fontana, California	1,300,000	180,000
United States Steel Corporation, Geneva, Utah	900,000	162,000

TABLE 7. (contd)

AISI Steelmaking District, Company and Location	Estimated Annual Sinter Capacity net tons	Estimated Annual Off-Gas Production million cubic feet
<u>Chicago</u>		
Bethlehem Steel Corporation, Burns Harbor, Indiana	4,300,000	540,000
Inland Steel Company, East Chicago, Indiana	1,200,000	175,000
United States Steel Corporation, Gary, Indiana	6,700,000	860,000
Youngstown Sheet & Tube Company, Indiana Harbor, Indiana	1,200,000	153,000
Interlake, Incorporated, South Chicago, Illinois	750,000	131,000
Republic Steel Corporation, South Chicago, Illinois	400,000	54,000
United States Steel Corporation, South Chicago, Illinois	2,200,000	282,000
Wisconsin Steel Div., I-H Co., South Chicago, Illinois	500,000	43,000

TABLE 8. Composition of Sinter-Plant Off-Gas^(a)

Constituent	Value	Unit
CO	0.35	volume percent
CO ₂	2.67	volume percent
O ₂	12.94	volume percent
N ₂	70.13	volume percent
H ₂	13.92	volume percent
SO ₃	3.27	ppm
SO ₂	0.38	ppm
NO _x	46.03	ppm

(a) The off gas composition was determined after it was passed through a pollution-control device.

TABLE 9. Blast Furnaces in the United States

District	Company	Number	Hearth Diameter ft.-in.	Cubic Feet BF Gas 10 ⁶
Northeast	Alan Wood Steel Company	1	19	432,709
	Swedeland, Pa.	1	18-0	
	Bethlehem Steel Corporation	1	24-0	
	Bethlehem, Pa.	1	27-11	
		2	30-0	
	U.S. Steel Corporation	1	29-6	
	Fairless, Pa.	2	30-10	344,320
	Bethlehem Steel Corporation	2	19-9	
	Sparrows Point, Md.	2	25-6	
		2	28-0	
		1	28-0	
		3	30-0	
Pittsburgh	Bethlehem Steel Corporation	1	21-3	972,636
	Johnstown, Pa.	1	22-8	
		1	26-0	
		1	26-0	
		1	28-0	
	Crucible Steel Corporation	1	19-0	
	Midland, Pa.	1	26-0	
	Jones & Laughlin Steel Corp.	1	27-3	
	Aliquippa, Pa.	1	28-6	
		1	28-6	
		1	29-0	
	Pittsburgh, Pa.	1	20-6	
		1	26-6	
		1	29-0	
	Shenango, Incorporated	1	27-0	
	Pittsburgh, Pa.	1	22-0	
	U.S. Steel Corporation	1	20-0	
	Duquesne, Pa.	1	23-0	
		1	24-6	
		1	28-0	
	Braddock, Pa.	1	23-6	
	(Edgar-Thompson-Irvin)	1	25-0	
		1	26-0	
		2	28-10	
	Rankin, Pa. (Homestead)	1	23-0	
		2	23-6	
		2	29-6	
	McKeesport, Pa. (National)	1	22-5	
		1	25-0	
	Wheeling-Pittsburgh Steel	1	19-0	
	Corporation	1	19-0	
	Monessen, Pa.	1	28-0	

TABLE 9. (contd)

District	Company	Number	Hearth Diameter ft.-in.	Cubic Feet BF Gas 10 ⁶
	National Steel Corporation	2	25-6	374,892
	Weirton, W.Va.	1	27-0	
	Steubenville, Ohio	1	21-2	
		1	23-9	
		1	24-0	
		1	24-9	
		1	25-0	
Buffalo	Bethlehem Steel Corporation	1	21-3	342,690
	Lackawanna, N.Y.	1	26-0	
		1	27-0	
		1	29-0	
		1	29-6	
		1	29-11	
	Republic Steel Corporation	1	21-6	
	Buffalo, N.Y.	1	22-9	
	National Steel Corporation	1	15-2	
	Buffalo, N.Y.	1	16-3	
		1	19-11	
Cleveland	Republic Steel Corporation	1	27-0	318,812
	Cleveland, Ohio	1	27-0	
		2	29-6	
	Jones & Laughlin Steel	1	26-6	
	Corporation	1	30-6	
	Cleveland, Ohio			144,464
	U.S. Steel Corporation	1	26-0	
	Cleveland, Ohio			
	Lorain, Ohio	1	23-0	
		1	23-6	
		1	23-8	
		1	28-6	
		1	29-0	
Youngstown	Republic Steel Corporation	1	26-3	370,886
	Youngstown, Ohio	1	26-3	
	Warren, Ohio	1	28-0	
	Sharon Steel Corporation	2	23-1	
	Farrell, Pa.			
	U.S. Steel Corporation	1	23-0	
	Youngstown, Ohio	2	25-0	
		1	26-3	
	Youngstown Sheet & Tube Company	1	16-0	
	Youngstown, Ohio	1	20-0	
	Campbell, Ohio	1	22-1	
		1	22-5	
		1	23-9	
		1	24-6	

TABLE 9. (contd)

District		Number	Hearth Diameter ft.-in.	Cubic Feet BF Gas 10 ⁶
Detroit	Ford Motor Company	1	20-0	508,430
	Dearborn, Michigan	1	20-0	
		1	29-0	
	McLouth Steel Corporation			
	Trenton, Michigan	2	30-0	
	National Steel Corporation	1	29-0	
	Ecorse, Michigan	1	29-0	24,626
		1	29-6	
		1	32-0	
	Interlake	1	21-0	
	Toledo, Ohio			
Cincinnati	Armco Steel Corporation	1	28-9	175,572
	Ashland, Kentucky	1	33-5	
	Detroit Steel Corporation	1	29-3	
	Portsmouth, Ohio			136,090
	Armco Steel Corporation	1	18-6	
	Hamilton, Ohio	1	19-6	
	Middletown, Ohio	1	29-6	
Southern	Armco Steel Corporation	1	27-3	92,672
	Houston, Texas			
	Lone Star Steel Company	1	27-3	
	Lone Star, Texas			242,801
	Republic Steel Corporation	1	17-0	
	Gadsen, Alabama	1	26-0	
	U.S. Steel Corporation	1	21-6	
	Fairfield, Alabama	1	22-0	
		1	22-6	
		2	25-0	
	U.S. Pipe and Foundry, Inc.	1	25-0	
	Birmingham, Alabama			
St. Louis	Granite City Steel Company	1	27-3	91,946
	Granite City, Illinois	1	28-0	
Western	C.F. & I. Steel Corporation	1	21-0	65,035
	Pueblo, Colorado	3	26-6	
	Kaiser Steel Corporation	2	27-0	161,292
	Fontana, California	1	27-0	
		1	29-6	
	U.S. Steel Corporation	3	26-6	124,536
	Geneva, Utah			

TABLE 9. (contd)

District		Number	Hearth Diameter ft.-in.	Cubic Feet BF Gas 10 ⁶
Chicago	Bethlehem Steel Corporation Burns Harbor, Indiana	1	38-3	1,087,621
		1	35-0	
		1	19-9	
		1	20-9	
		1	20-9	
		1	21-6	
		1	26-6	
		2	26-6	
		1	26-6	
	U. S. Steel Corporation Gary, Indiana	1	20-6	
		2	20-6	
		1	20-6	
		1	23-0	
		2	25-0	
		1	26-6	
		1	27-0	
		1	28-0	
		1	28-0	
		1	28-3	
	Youngstown Sheet & Tube Company Indiana Harbor, Indiana	1	40-4	
		1	22-9	
		1	27-6	
		1	29-6	
	Wisconsin Steel Division, I-H. South Chicago, Illinois	1	32-0	
		1	18-9	
		1	20-3	
		1	23-0	
	Interlake Steel Corporation Chicago, Illinois	1	19-8	409,842
		1	25-9	
	Republic Steel Corporation Chicago, Illinois	1	28-0	
		1	28-0	
	U.S. Steel Corporation South Chicago, Illinois	2	21-6	
		1	22-3	
		1	23-0	
		1	25-3	
		1	25-9	
		2	29-0	

TABLE 10. Typical Compositions of Blast-Furnace Gas

Heating Value Btu/ft ³	Constituents, volume percent			
	CO	CO ₂	H ₂	N ₂
80	22.3	18.2	3.0	56.5
90	22.5	16.3	5.5	54.9
100	27.2	13.6	4.5	54.7

blown into the blast furnace, oxygen enrichment of the blast air, and the injection of hydrocarbons through the tuyères. Today's blast-furnace practice tends to produce a blast-furnace top-gas with between 80 and 85 Btu/ft³.

About one-third of the blast-furnace gas produced is used to heat the blast stoves, which preheat air before it is blown into a blast furnace. Blast-furnace gas is also used for heating soaking pits, annealing furnaces, and other miscellaneous uses in a steel plant. The total amount of blast-furnace gas estimated in Table 9 is 6,421,872 million ft³. The American Iron and Steel Institute⁽¹⁶⁵⁾ reported 5,027,796 million ft³ consumed in 1973, which is 78% of the estimated amount. A recent study,⁽¹⁶⁶⁾ released by the Environmental Protection Agency, reported that about 20% of the blast-furnace gas produced in the U.S. steel industry is flared or wasted, which agrees closely with the 78% usage figure reported for 1973.

Direct Reduction of Iron Ore

Direct processes for reducing iron ore without blast furnaces are becoming increasingly important as a small-scale method especially in under-developed countries. Current capacity of these direct processes is 33 million tons/yr with 20 million tons/yr of capacity under construction. The two processes receiving the most interest are countercurrent flow reactor-type processes in which iron ore pellets fall down through the hot reactor as the reducing gases move upward. The gas requirement now generally comes from steam reformed natural gas and involves 14 to 18 million Btu/ton of sponge iron produced. Scrubbed coal gas or other fuel or waste gases as the reductant is now under study. Direct reduction of iron ore to iron has been proposed, using CO produced from partial combustion of a carbonaceous fuel. The off-gas from this would be used to make ammonia.⁽¹⁶⁷⁾ Carbon monoxide utilization would involve about 2 tons of CO per ton of sponge iron. With the approximate minimum size of direct reduction units at 100,000 tons/yr, a source of 200,000 tons/yr of CO would be required.

Basic-Oxygen Steelmaking Furnaces

The major process for converting pig iron into steel is the basic-oxygen furnace. The off-gas composition at the mouth of the BOF vessel is quite high in CO. Typical composition range of the off-gas is given in

Table 11. Air pollution control for BOF steelmaking furnaces is accomplished with wet scrubbers and electrostatic precipitators; about half of the BOF's use scrubbers and the other half electrostatic precipitators. Except for two BOF shops, all burn the off-gas prior to cleaning. Combustion is encouraged to prevent serious explosions in the air pollution control equipment, especially for those BOF's using electrostatic precipitators. The data given in Table 12 shows the off-gas volume produced by combustion. Typical composition of the off-gas after combustion is given in Table 13. In recent years, air pollution control systems have been developed to suppress combustion of the off-gas. One system developed in France is called the "IRSID-CAFL System,"⁽¹³⁴⁾ and another developed in Japan is called the "OG System."^(132,133) A typical composition of the off-gas for suppressed-combustion pollution control systems is given in Table 14. The volume of gases produced by suppressed-combustion will vary between 5 to 10% of the values shown in Table 12. The variation is influenced by the composition of the charge, oxygen blowing rate, and air-tightness of the gas-collection system for pollution control. The two BOF steelmaking plants in the United States that have suppressed-combustion air pollution control systems are the Armco Steel Corporation plant in Middletown, Ohio, and the United States Steel Corporation plant in Lorain, Ohio. One of Inland Steel Company's BOF shops in East Chicago, Indiana, was built to accept such a system at a later time. Kaiser steel has a BOF shop under construction with completion scheduled for 1978.

TABLE 11. Composition of BOF Off-Gas at BOF Vessel

<u>Constituent</u>	<u>Volume Percent</u>
CO	58 - 64
CO ₂	15 - 18
N ₂	19 - 22
O ₂	1 - 2

TABLE 12. Basic Oxygen Furnace Steelmaking Plants

AISI Steelmaking District, Company and Location	Estimated Annual Capacity Net Tons	Estimated Annual Off-Gas Production After Combustion Million Cubic Feet
<u>Northeast</u>		
Alan Wood Steel Company Swedeland, PA	1,250,000	56,500
Bethlehem Steel Corporation Bethlehem, PA	2,500,000	120,400
Sparrows Point, MD	2,500,000	120,400
<u>Pittsburgh</u>		
A-L Industries, Incorporated Natrona, PA	500,000	33,300
Bethlehem Steel Corporation Johnstown, PA	2,500,000 ^(a)	120,400
Crucible Steel Corporation Midland, PA	1,250,000	35,700
Jones & Laughlin Steel Corporation Aliquippa, PA	3,000,000	137,000
Sharon Steel Corporation Farrell, PA	1,300,000	61,200
United States Steel Corporation Braddock, PA	2,750,000	124,200
Duquesne, PA	2,500,000	125,000
Wheeling-Pittsburgh Steel Corporation Monessen, PA	1,500,000	85,200
National Steel Corporation Weirton, WV	3,400,000	175,000
Wheeling-Pittsburgh Steel Corporation Steubenville, OH	2,000,000	111,600
<u>Buffalo</u>		
Bethlehem Steel Corporation Lackawanna, NY	4,700,000	206,300
Republic Steel Corporation Buffalo, NY	1,000,000	40,600
<u>Cleveland</u>		
Jones & Laughlin Steel Corporation Cleveland, OH	2,250,000	89,000
Republic Steel Corporation Cleveland, OH	2,250,000	141,300
United States Steel Corporation Lorain, OH	2,250,000	119,700
<u>Youngstown</u>		
Republic Steel Corporation Warren, OH	1,600,000	117,000
Sharon Steel Corporation Farrell, PA	1,300,000	61,200
Youngstown Sheet & Tube Company Youngstown, OH	2,500,000 ^(b)	125,000

TABLE 12. (Cont'd)

AISI Steelmaking District, Company and Location	Estimated Annual Capacity Net Tons	Estimated Annual Off-Gas Production After Combustion Million Cubic Feet
<u>Cincinnati</u>		
Armco Steel Corporation		
Middletown, OH	2,000,000	96,000
Ashland, KY	1,700,000	90,700
<u>Southern</u>		
Republic Steel Corporation		
Gadsden, AL	1,500,000	74,200
United States Steel Corporation		
Fairfield, AL	1,500,000	74,000
<u>Chicago</u>		
Bethlehem Steel Corporation		
Burns Harbor, IN	4,000,000	175,500
Inland Steel Company		
East Chicago, IN (No. 2 BOF)	2,000,000	94,300
(No. 4 BOF)	4,000,000	174,500
United States Steel Corporation		
Gary, IN (No. 1 BOF)	3,700,000	207,800
(No. 2 Q-BOF)(c)	5,000,000	275,000
Youngstown Sheet & Tube Company		
Indiana Harbor, IN	2,400,000	96,000
Interlake, Incorporated		
Chicago, IL	730,000	36,400
Republic Steel Corporation		
S. Chicago, IL	1,200,000(c,d)	60,000
United States Steel Corporation		
S. Chicago, IL	3,000,000	175,000
Wisconsin Steel Division, I-H Co.		
S. Chicago, IL	1,200,000	60,000
<u>Detroit</u>		
Ford Motor Company, Steel Division		
Dearborn, MI	2,500,000	130,100
McLouth Steel Corporation		
Trenton, MI	2,800,000	157,000
National Steel Corporation		
Ecorse, MI (No. 1 BOF)	3,500,000	144,200
(No. 2 BOF)	2,000,000	83,000
<u>St. Louis</u>		
National Steel Corporation		
Granite City, IL	2,200,000	87,100
<u>Western</u>		
CF&I Corporation		
Pueblo, CO	1,100,000	52,800
Kaiser Steel Corporation		
Fontana, CA	1,440,000	69,300
	2,300,000(e)	110,000

(a) To be started up in 1978.

(b) To be started up in 1977.

(c) Q-BOF is a bottom blown steelmaking process.

(d) To be started up in 1977.

(e) New BOF Shop to replace openhearth shop by 1978.

TABLE 13. Composition of BOF Off-Gas After Combustion

<u>Constituent</u>	<u>Volume Percent</u>
CO	0.0 - 0.3
CO ₂	0.7 - 13.5
O ₂	11.1 - 20.0
N ₂	74.5 - 78.9
H ₂	0.0 - 0.4
Illuminants	0.0 - 0.2

TABLE 14. Composition of BOF Off-Gas with Suppressed Combustion

<u>Constituent</u>	<u>Volume Percent</u>
CO	50.0 - 68.5
CO ₂	19.0 - 28.0
N ₂	6.5 - 19.7
H ₂	2.2 - 5.0
O ₂	0.1 - 1.0

Open-Hearth Furnaces

Open-hearth furnace steelmaking has declined from its position as the dominant steelmaking process to third in rank. In 1970, open-hearth steelmaking fell below BOF steelmaking in annual production, and 1975 it also fell below electric-arc furnace steelmaking. Open-hearth steelmaking cannot be considered a source of CO because it uses excess air to burn the fuels for melting and refining the steel. Combined with the open-hearth furnace, the regenerative-checker heating system, and the air pollution control system, survival of CO is precluded. The U.S. Environmental Protection Agency does not list CO from open-hearth furnaces as an environmental pollutant, and has

not reported any CO values for open-hearth gas analyses. The furnaces listed in Table 15 are given to complete the picture on the steel industry's melting units, and also to indicate those open-hearth steelmaking plants that are scheduled for replacement in the near future.

Electric-Arc Steelmaking Furnaces

An increasingly common type of steelmaking furnace is the electric-arc furnace. Electric furnaces and their locations are given in Table 16. A major problem in attempting to utilize CO from electric-arc steelmaking furnaces is the air pollution control systems used with the furnaces, which all depend on combustion of the exhaust gases coming from the furnaces, to prevent explosions in the systems. Four general types of systems are used in controlling electric-arc furnace emissions: 1) direct extraction, 2) furnace hoods, 3) roof canopy hoods, and 4) building evacuation. There may also be combinations of these systems. Furnace hoods, roof canopies, and building evacuation each expose the exhaust gases to excess air around the furnace proper or in the building interior, with the result that little CO exists in the off-gas. Values of 0 to 6% have been reported in the exhaust systems, depending on the type of steel being made and the related pollution-control system. Analyses for 22 net ton heats of steel showed about 130 ft³ of CO produced per net ton of low-alloy steel, and about 320 ft³ of CO generated per net ton of stainless steel.

Gray Iron Castings

The production of gray iron castings is an extremely diverse and dispersed industrial process. Gray iron castings include the great variety of light and heavy machinery parts made of cast iron such as truck, automobile and farm machinery engines, blocks, housings, pump and turbine parts, machinery frames, mountings, molded forms, sewer pipe and many forms of plumbing and pipe fittings. The total production exceeds 10 million tons/yr. Except for the major machinery manufacturing plants, most production takes place in hundreds of relatively small foundries distributed throughout the country. Although various types of cast iron are produced (gray iron, modular iron and malleable iron) the production process is fairly uncomplicated.

TABLE 15. Open Hearth Steelmaking Plants

AISI Steelmaking District, Company and Location	Estimated Annual Capacity net tons
<u>Northeast</u>	
Bethlehem Steel Corporation, Sparrows Pt., Maryland	3,500,000
Phoenix Steel Corporation Phoenixville, Pennsylvania	600,000
Unites States Steel Corp., Fairless, Pennsylvania	3,500,000
<u>Pittsburgh</u>	
Bethlehem Steel Corporation Johnstown, Pennsylvania	2,300,000 ^(a)
Harrisburg Steel Company, Harrisburg, Pennsylvania	150,000
Jones & Laughlin Steel Corp., Pittsburgh, Pennsylvania	3,000,000 ^(b)
United States Steel Corp., Homestead, Pennsylvania	3,250,000
<u>Buffalo</u>	
Bethlehem Steel Corporation, Lackawanna, New York	1,000,000 ^(c)
<u>Youngstown</u>	
United States Steel Corp., Youngstown, Ohio	1,500,000
Youngstown Sheet and Tube Co., Campbell, Ohio	1,100,000
Youngstown, Ohio	1,500,000 ^(d)
<u>Cincinnati</u>	
Armco Steel Corporation, Middletown, Ohio	1,250,000
<u>Southern</u>	
United States Steel Corp., Fairfield, Alabama	2,500,000

(a) To be replaced by 2-vessel BOF shop in 1978

(b) To be replaced by electric-arc furnace shop in 1977

(c) Is operated intermittently.

(d) To be replaced by 2-vessel BOF shop in 1977

TABLE 15. (Contd)

AISI Steelmaking District, Company and Location	Estimated Annual Capacity net tons
<u>Chicago</u>	
Inland Steel Company, East Chicago, Indiana	2,000,000
Republic Steel Corporation, S. Chicago, Illinois	800,000 ^(e)
Youngstown Sheet & Tube Company, Indiana Harbor, Indiana	2,500,000
<u>Western</u>	
Kaiser Steel Corporation, Fontana, California	1,500,000 ^(f)
Pacific States Steel Company Union City, California	275,000
United States Steel Corporation Torrance, California	125,000
Geneva, Utah	3,500,000

(e) To be replaced by 2-vessel Q-BOP shop in 1977.

(f) To be replaced by 2-vessel BOF shop in 1978.

TABLE 16. Electric-Arc Furnace Steelmaking Plants and Estimated Off-Gas Production

AISI Steelmaking District, Company and Location	Furnaces number	Estimated Annual Capacity net tons	Estimated Annual Off-Gas Production million cubic feet
<u>Northeast</u>			
Allegheny Ludlum Industries, Inc. Watervliet, New York	3	100,000	1,000
Armco Steel Corporation, Baltimore, Maryland	3	110,000	2,600
Bethlehem Steel Corporation, Bethlehem, Pennsylvania	5	300,000	90
Steelton, Pennsylvania	3	1,400,000	2,300
B-L-H Corporation, Burnham, Pennsylvania	4	240,000	80
Carpenter Technology Corporation, Bridgeport, Connecticut	2	70,000	100
Reading, Pennsylvania	5	108,000	
Ceco Corporation, Milton, Pennsylvania	3	170,000	420
EASCO Corporation, Baltimore, Maryland	3	120,000	1,100
Lukens Steel Company, Coatesville, Pennsylvania	4	800,000	3,400
Midvale-Heppenstall Company, Philadelphia, Pennsylvania	3	150,000	60
New Jersey Structural Steel Corp., Sayerville, New Jersey	2	250,000	550
Phoenix Steel Corporation, Claymont, Delaware	2	500,000	1,200
United States Steel Corporation, Fairless, Pennsylvania	2	550,000	1,500
Washburn Wire Company, Phillipsdale, Rhode Island	2	120,000	750
<u>Buffalo</u>			
Auburn Steel Company Auburn, New York	1	170,000	420
Crucible, Incorporated, Syracuse, New York	5	70,000	95
National Forge Company, Erie, Pennsylvania	3	150,000	55
Irvine, Pennsylvania	2	75,000	40
Roblin Industries, Inc., Dunkirk, New York	2	150,000	400
Wallace Murray Corporation, Lockport, New York	3	55,000	300

TABLE 16. (Contd)

AISI Steelmaking District, Company and Location	Furnaces Number	Estimated Annual Capacity net tons	Estimated Annual Off-Gas Production million cubic feet
<u>Pittsburgh</u>			
A-L Industries, Incorporated Brackenridge, Pennsylvania	4	350,000	5,000
Armco Steel Corporation Butler, Pennsylvania	3	1,000,000	20,000
Babcock and Wilcox Company Beaver Falls, Pennsylvania	4	250,000	550
Koppel, Pennsylvania	5	460,000	1,100
Braeburn Alloy Steel Corporation Braeburn, Pennsylvania	2	50,000	900
Crucible Steel Corporation Midland, Pennsylvania	5	250,000	4,000
Cyclops Corporation Bridgeville, Pennsylvania	3	120,000	2,700
Edgewater Corporation Oakmont, Pennsylvania	1	80,000	950
Latrobe, Pennsylvania	1	70,000	950
Electralloy Corporation Oil City, Pennsylvania	1	60,000	800
Jessop Steel Company Washington, Pennsylvania	4	100,000	900
Jones & Laughlin Steel Corporation Pittsburgh, Pennsylvania	2(a)	1,700,000	100,000
Mesta Machine Company West Homestead, Pennsylvania	2	200,000	70
Teledyne Mid-America Corporation Latrobe, Pennsylvania	1	30,000	800
Monaca, Pennsylvania	1	35,000	800
Timken Company Latrobe, Pennsylvania	3	100,000	1,000
Union Electric Steel Corporation Burgettstown, Pennsylvania	1	75,000	95
United States Steel Corporation Duquesne, Pennsylvania	5	300,000	320
Johnstown, Pennsylvania	3	80,000	1,000
Washington Steel Corporation Houston, Pennsylvania	2	100,000	2,500
<u>Cleveland</u>			
Jones & Laughlin Steel Corporation Cleveland, Ohio	2	1,000,000	5,300
<u>Youngstown</u>			
Armco Steel Corporation Marion, Ohio	2	400,000	900
Copperweld Corporation Warren, Ohio	5	700,000	450

TABLE 16. (Contd)

AISI Steelmaking District, Company and Location	Furnaces Number	Estimated Annual Capacity net tons	Estimated Annual Off-Gas Production million cubic feet
Cyclops Corporation Mansfield, Ohio	2	400,000	900
Republic Steel Corporation Canton, Ohio	9	1,000,000	30,000
Warren, Ohio	2	450,000	4,000
Sharon Steel Corporation Roemer, Pennsylvania	2	400,000	1,200
Timken Company Canton, Ohio	8	1,200,000	3,000
<u>Cincinnati</u>			
Athlone Industries, Inc. Owensboro, Kentucky	2	200,000	1,400
American Compressed Steel Company Cincinnati, Ohio	1	13,000	250
BW Steel, Incorporated New Castle, Indiana	4	60,000	300
Interlake, Incorporated Newport, Kentucky	3	480,000	1,900
Kentucky Electric Steel Company Coalton, Kentucky	3	180,000	450
H. K. Porter Company, Inc. Huntington, West Virginia	2	300,000	600
<u>Detroit</u>			
A-L Industries, Incorporated Ferndale, Michigan	2	8,000	800
Ford Motor Company, Steel Division Dearborn, Michigan	2	750,000	3,000
General Motors Corporation Flint, Michigan	3	100,000	350
Jones & Laughlin Steel Corporation Warren, Michigan	5	750,000	16,000
McLouth Steel Corporation Trenton, Michigan	2	480,000	8,000
Michigan Seamless Tube Company Jackson, Michigan	2	180,000	450
National Steel Corporation Ecorse, Michigan	2	750,000	3,200
<u>Southern</u>			
Intercoastal Steel Corporation Chesapeake, Virginia	2	100,000	350
Roanoke Electric Steel Corporation Roanoke, Virginia	3	170,000	400

TABLE 16. (Contd)

AISI Steelmaking District, Company and Location	Furnaces Number	Estimated Annual Capacity net tons	Estimated Annual Off-Gas Production million cubic feet
Florida Steel Corporation			
Croft, North Carolina	2	140,000	370
Georgetown Steel Corporation			
Georgetown, South Carolina	3	500,000	1,200
NUCOR Corporation			
Darlington, South Carolina	3	200,000	450
Owen Electric Steel Company			
Cayce, South Carolina	3	100,000	350
Atlantic Steel Company			
Atlanta, Georgia	2	450,000	530
Cartersville, Georgia	1	180,000	250
Florida Steel Corporation			
Baldwin, Florida	1	180,000	400
Indiantown, Florida	2	170,000	400
Tampa, Florida	3	270,000	600
Ceco Corporation			
Birmingham, Alabama	2	85,000	300
H.K. Porter Company, Inc.			
Birmingham, Alabama	2	300,000	650
Republic Steel Corporation			
Gadsden, Alabama	2	450,000	1,000
Magma Corporation			
Flowood, Mississippi	3	180,000	250
Azcon Corporation			
Knoxville, Tennessee	2	200,000	450
Tennessee Forging Steel Corporation			
Harriman, Tennessee	3	230,000	500
Armco Steel Corporation			
Houston, Texas	6	1,800,000	33,000
Border Steel Mills, Inc.			
Vinton, Texas	2	144,000	370
Cabot Corporation			
Pampa, Texas	1	27,000	800
Cameron Iron Works, Inc.			
Houston, Texas	2	120,000	250
Chaparral Steel Company			
Midlothian, Texas	1	300,000	600
Georgetown Steel Corporation			
Beaumont, Texas	2	500,000	1,200
Marathon-LeTourneau Company			
Longview, Texas	2	100,000	300
NUCOR Corporation			
Jewett, Texas	2	250,000	550
Commercial Metals Company			
Seguin, Texas	2	180,000	400
Texas Steel Company			
Fort Worth, Texas	2	200,000	450
United States Steel Corporation			
Baytown, Texas	4	2,000,000	6,000

TABLE 16. (Contd)

AISI Steelmaking District, Company and Location	Furnaces Number	Estimated Annual Capacity net tons	Estimated Annual Off-Gas Production million cubic feet
Armco Steel Corporation Sand Springs, Arkansas	2	300,000	570
Tennessee Forging Steel Corporation Newport, Arkansas	2	150,000	400
Ross Steel Works, Incorporated Amite, Louisiana	2	100,000	300
<u>Chicago</u>			
Inland Steel Company East Chicago, Indiana	2	500,000	1,200
Joslyn Manufacturing & Supply Company Fort Wayne, Indiana	4	60,000	900
Penn-Dixie Steel Corporation Kokomo, Indiana	2	600,000	1,700
Cabot Corporation Kokomo, Indiana	2	25,000	800
California Steel Company Chicago, Illinois	1	100,000	300
Cargill, Incorporated St. Paul, Minnesota	2	400,000	900
Ceco Corporation Lemont, Illinois	3	220,000	500
Columbia Tool Steel Company Chicago Heights, Illinois	2	20,000	800
Finkl and Sons Company Chicago, Illinois	2	200,000	1,400
ITT Harper Morton Grove, Illinois	2	20,000	800
Northwestern Steel & Wire Company Sterling, Illinois	4	2,000,000	6,000
Republic Steel Corporation South Chicago, Illinois	3	750,000	16,000
Tennessee Forging Steel Corporation Kankakee, Illinois	2	100,000	300
United States Steel Corporation South Chicago, Illinois	3	800,000	1,050
<u>St. Paul</u>			
Armco Steel Corporation Kansas City, Missouri	4	1,000,000	1,800
Cargill, Incorporated Wilton, Iowa	1	150,000	400
Keystone Consolidated Industries Peoria, Illinois	2	600,000	1,700
Laclede Steel Company Alton, Illinois	2	450,000	400
NUCOR Corporation Norfolk, Nebraska	2	250,000	550

TABLE 16. (Contd)

AISI Steelmaking District, Company and Location	Furnaces Number	Estimated Annual Capacity net tons	Estimated Annual Off-Gas Production million cubic feet
<u>Western</u>			
CF&I Corporation Pueblo, Colorado	2	600,000	1,600
Marathon Manufacturing Company Tempe, Arizona	3	180,000	450
Cascade Steel Rolling Mills, Inc. McMinnville, Oregon	2	130,000	350
Gilmore Steel Corporation Portland, Oregon	2	400,000	900
Bethlehem Steel Corporation Seattle, Washington	2	500,000	400
Earle M. Jorgensen Company Seattle, Washington	2	120,000	50
N.W. Steel Rolling Mills, Inc. Seattle, Washington	2	240,000	500
Hawaiian Western Steel, Ltd. Ewa, Hawaii	1	50,000	300
Ameron, Incorporated Etiwanda, California	4	350,000	750
Armco Steel Corporation Torrance, California	2	60,000	300
Bethlehem Steel Corporation Los Angeles, California	3	350,000	920
Judson Steel Corporation Emeryville, California	1	100,000	300
Soule Steel Company Long Beach, California	2	150,000	400
S.W. Steel Rolling Mills, Inc.(b) Los Angeles, California	2	100,000	300
Whitteman Steel Mills Fontana, California	1	40,000	250

(a) Start-up in 1978.

(b) Not operating.

It involves charging a vertical shaft furnace called a cupola with coke fuel and mostly recycled scrap iron with or without certain alloying agents. The cupola is heated to the temperature at which the combustion of the coke with air, which may be slightly enriched with oxygen, produces the molten iron which is cast directly into the desired forms. The high temperature of the process together with the control of air delivery results in a flue gas in which the CO content may be about 15% by volume; the CO₂ will be about one-half to two-thirds as concentrated. Large cupolas, perhaps several in parallel, produce 50 to 60 tons of melt per hour and discharge as much as 7 tons of CO per hour in the form of 15% gas. Some of this is recycled as fuel for combustion air heating but most is cleaned of particulates and directly vented without flaring.

Some of the largest foundries may be discharging a few hundred thousand tons of CO per year. Coupling of a practical and economical concentration process to these sources could lead to significant conservation results when processed to ammonia or methanol.

FERRO ALLOYS

The ferro-alloy industry produces ferro-silicon (FeSi), ferro-chrome (FeCr), ferro-manganese (FeMn), silico-manganese (SiMn), ferro-chrome-silicon (FeCrSi) and other minor alloys such as ZrSi, CrSi, FeMo, FeNi, FeCb, and FeV. Some production data are shown in Table 17. Production sites are shown in Figure 3.

With few exceptions, these materials are all made in submerged-arc electrical resistance furnaces. The important exceptions are FeMn, produced in blast furnaces, and FeP, produced in elemental phosphorus electric furnaces (discussed later in this report). The alumino-thermic process for production of FeMo, FeCb, FeV, FeB, and FeTi does not produce CO and will not be mentioned further here.

All of these submerged-arc furnaces produce CO, but the configuration of the off-gas capture hood determines whether the CO is collectible or not. There are both open and sealed hoods, but only five furnaces in the U.S. do

TABLE 17. Ferroalloys Produced and Shipped from
Furnaces in the United States

	<u>Production-1973</u> <u>Gross Weight</u> <u>(Short Tons</u> <u>x 10³)</u>
Ferromanganese ^(a)	683
Silicomanganese	183
Ferrosilicon ^(b)	877
Silvery Pig Iron	135
Chromium Alloys:	
Ferrochromium:	
High-Carbon	241
Low-Carbon	88
Ferrochromium:	
Silicon	80
Other Alloys ^(c)	<u>16</u>
Total	426
Ferrotitanium	1
Ferrophosphorus	129
Ferrocolumbium	1
Other ^(d)	<u>80</u>
Grand Total	2,519

(a) Includes briquets and fused-salt electrolytic.

(b) Includes silicon metal and inoculant type alloys.

(c) Includes chromium briquets, chromium metal, exothermic chromium additives, and other miscellaneous chromium alloys.

(d) Includes ferroboration, ferronickel, ferromolybdenum, ferrotungsten, ferrovanadium, spiegeleisen, ferrozirconium, and other miscellaneous alloys.

FIGURE 3. Ferro-Alloys

not have open hoods. The open hood allows for visual contact and operation of the furnace; any required stoking can be handled easily, charging of feed materials can be easily accomplished and the combustible gas, CO, is burned quickly and effectively at the surface of the burden. Of the closed hood furnaces, only one has a mechanically sealed system; that being Airco's Mobile, Alabama, plant. Union Carbide has four plants with semi-sealed furnaces, in which the charge itself provides the seal, two of which produce a concentrated CO stream. The two other plants could produce similar streams with some capital improvements to repair worn equipment and pollution controls. They do not at this time, due to lack of use for the CO. These semi-sealed furnaces will likely no longer be built because they have the limited flexibility of a sealed furnace without the near perfect control of the off-gas.

Although approximately 1.3 million tons of CO are produced annually in ferro-silicon production alone, the use of open hooded furnaces makes recovery of this by-product impossible. There is little incentive for closed furnaces. U.S. EPA pollution standards require only that dust be cleaned from the waste gas before being exhausted to the atmosphere.⁽¹⁶⁸⁾ In order to produce CO as a useful by-product from closed furnaces, major modifications would be required in the furnace structure and/or the production routine. To build a closed-hood furnace with an operating procedure similar to the open-hood furnace, mechanically-sealed stirring paddles would be installed through the hood, a viewing glass would have to be installed and the charge would have to enter in a plug-flow or lock-hopper type of system. The other option, which is used in sealed furnaces in Europe and Japan is to pre-treat the ore and size it to reduce the crusting tendency and thus the need for stoking.

A blast furnace operation to produce ferro-manganese is used by U.S. Steel and Bethlehem Steel. Only one of these facilities is presently operating, but it produces over 600 thousand tons of CO per year; 88% of it is burned to recover the Btu value, and the rest is flared.

The application of CO utilization in the ferro-alloy industry appears limited until new techniques and innovations are available. There are several sources of CO available, but these are not in the mainstream of the developing technology. Table 18 lists only those furnaces in the U.S. which produce recoverable CO.

TABLE 18. Ferro-alloy Furnaces Which are Potential Sources of Carbon Monoxide

<u>Company</u>	<u>Location</u>	<u>Furnace Type</u>	<u>Product</u>
Airco Alloys & Carbide	Mobile, AL	sealed furnace	SiMn
Bethlehem Steel Corp	Johnstown, PA	blast furnace	FeMn
Union Carbide Corp	Ashtabula, OH	semi-sealed furnaces	
	Sheffield, AL	semi-sealed furnace	Fe --
	Marietta, OH	open and semi-sealed furnaces	FeMn, FeCr
	Portland, OR	semi-sealed operated as open furnace	FeMn

ALUMINUM

Aluminum metal is produced entirely by an energy-intensive electrolytic process, although chemical reduction in a blast furnace has been proposed as a method of making aluminum silicon alloy.⁽¹⁶⁹⁾ In 1975, the installed capacity in the U.S. was about 4.9 million tons/yr. Plant sizes are normally about 100,000 tons/yr capacity.

Process

The process flow-chart is shown in Figure 4. Aluminum is produced by electrolysis of pure aluminum oxide (alumina) in a bath of liquid cryolite (Na_3AlF_6) containing some excess aluminum fluoride (AlF_3) and 6 to 10% of

FIGURE 4. Cross-Section of an Aluminum Production Cell

fluorspar (CaF_2). The alumina concentration is about 2 to 6%. The cathode is a steel bath lined with impure carbon and the anode is also of carbon. Aluminum is produced at the cathode, and oxygen at the anode. The oxygen combines with the carbon of the anode to produce a mixture of CO_2 and CO :

In most of the aluminum cells in the U.S., the CO off-gas is exposed to air and is completely oxidized to CO_2 . While this meets clean air standards, it represents a considerable waste of CO . The availability of off-gas containing CO depends on the configuration of the electrolytic cell.

Three types of reduction cells (pots) are utilized in the aluminum industry. The principal differences between the cells involve the type of anode used and the method of connecting the anode to the busbar. The three types of anodes employed are the vertically pinned Soderberg (Pechiney), the horizontal pinned Soderberg and the prebaked anode.

The Soderberg anodes are called continuously baking anodes. Briquettes formed from petroleum coke and hard pitches are charged to a metal anode shell; as the charge progresses through the shell the temperature from the molten bath in the cell is high enough to fuse and bake the briquettes into a solid block. The volatile matter from the briquettes distills off in the process.

The prebaked anode process employs anodes which are formed and baked in a separate facility. This is the preferred process for new aluminum plants because the cell off-gases from this process are much cleaner (the volatile organics having been removed during the prebaking) than from the Soderberg processes. The cleaner off-gases meet air quality standards inside the pot line buildings more easily.

The physical orientation of the vertically pinned Soderberg anode allows the anode to be surrounded by a metal sheath which acts as a conduit for the gases formed in the cell. This arrangement results in a high CO concentration since the cell off-gas is not exposed to air.

The off-gases from the horizontally pinned Soderberg and prebaked anode cells exit the cell through holes in the alumina crust floating at the surface of the cell. The cells are covered with loosely fitting hoods which are maintained at a negative air pressure to facilitate collecting the off-gases, including fluorides and particulates. Carbon monoxide in the hot off-gases exiting the cell is burned to CO₂ by air coming in around the loosely fitting hood. Thus, only aluminum reduction cells employing the vertically pinned Soderberg anode have appreciable amounts of CO in the cell off-gases.

The off-gas from a vertically pinned Soderberg cell contains 25 to 35 volume percent CO (30 volume percent average). The remainder of the gas is essentially 99% CO₂ plus small amounts of tars, oils, and fluorides.

Current practice is to burn the off-gases by combining them with air in a burner before scrubbing to remove fluorides, etc. This practice eliminates the tars and oils from the gas stream before the scrubbing operation. An average of about 0.6 tons of anode carbon is consumed for each ton of aluminum produced. Approximately 34,000 scf of off-gases are produced during the production of 1 ton of aluminum. The five U.S. aluminum plants equipped with vertically pinned Soderberg anode reduction cells are listed below (Table 19). The table also lists the amount of CO produced when all facilities are operating at capacity, and the off-gases contain an average 30 volume percent CO.

TABLE 19. Sources and Estimated Quantities of Carbon Monoxide-Containing Off Gas from the U.S. Aluminum Industry (vertically pinned Soderberg cells only)

<u>Company</u>	<u>Location</u>	<u>Annual Aluminum Capacity (tons)</u>	<u>Potential Annual Carbon Monoxide Production (tons)</u>
Anaconda Aluminum	Columbia Falls, Montana	180,000	71,599
Alcoa	Alcoa, Tennessee	54,000	21,480
Alcoa	Point Comfort, Texas	180,000	71,599
Martin Marietta Aluminum Company	Goldendale, Washington	100,000	39,777
Martin Marietta Aluminum Company	The Dalles, Oregon	100,000	39,777
Totals		614,000	244,232

Figure 5 shows the U.S. distribution of aluminum production, with potential sources of CO off-gas marked.

FIGURE 5. Geographical Distribution of Aluminum Production

Prospects for Carbon Monoxide Recovery

For most U.S. aluminum producers, who do not use the Soderberg anode system, waste CO is burned in an excess of air drawn under the cell hood, and unless there is a real economic incentive for modification, recovery is unlikely to be performed. Currently, the oxide crust formed on the surface of the cell by the reaction of aluminum with air, carbon dioxide,⁽¹⁷⁰⁾ or CO, is periodically broken by mechanical means.⁽¹⁷¹⁾ Putting in a CO off-gas recovery system would interfere with this process.

The five producers using the vertically pinned Soderberg anode are in a much better position, since they normally collect the off-gas before burning it. A system for removing the tars and oils, the fluoride impurities in the gas,

and precipitating dust would be required. Although the vertically pinned Soderberg cell is the older system, strong economic incentives for using the large quantity of CO produced could swing the industry in favor of this cell again.

Contacts with the industry indicated that data on the actual off-gas composition are often poor and incomplete, although there are techniques available for measuring anode gas composition--gas chromatography, for example.⁽¹⁷²⁾

A relatively new process for aluminum production involves prior chlorination of the ore, forming aluminum chloride. This is then electrolyzed as liquid sodium aluminum chloride, to aluminum metal and recyclable chlorine:

This process does not produce by-product CO.

ZINC, TIN, LEAD AND COPPER

There are two processes for the production of zinc metal based on electrolytic deposition and thermal reduction with carbon (the distillation process). Electrolytic deposition does not generate CO, although CO is generated in zinc refining in electric furnaces.⁽¹⁷³⁾ Two U.S. zinc smelters use the distillation process at this time.

The traditional vertical retort process is used by the New Jersey Zinc Co., at Palmerton, PA. Zinc ore, coke, and flux are dumped at the bottom of a tall, vertical shaft which is heated at about 1000°C to distill off the zinc. The off-gas, after condensation of the zinc, contains CO and other non-condensibles, and is burned in jets on the sides of the retort. The gas is 75-90% CO (200-300 Btu) and provides about 25% of the needed firing power to heat the retort.

The electrothermic process is used by the St. Joe Mineral Corp., of Monaca, PA. This process also uses a vertical retort but is heated by electrical resistance. The off-gas is 80% CO with a heating value of 250 Btu/ft³.

About 75% of the off-gases are used for concentrate drying and preheating. The remainder is flared.

The approximate annual CO production by these two plants is:

Palmerton	72,000 tons/yr
Monaca	90,000 tons/yr.

If alternative fuels could be found (e.g., coal) to replace the CO for heating, this industry would represent a significant resource of CO.

In addition to the production of crude zinc by the carbon reduction method, purification in electric furnaces with carbon electrodes is also a source of waste CO.⁽¹⁷³⁾ However, electrolytic purification is normally used in the U.S. We are aware of no U.S. companies using an electrothermic zinc purification process at this time.

Production of recoverable CO in lead blast furnaces is small. One plant representative stated that gas containing 3.21% CO leaves the furnace at 65,000 cfm, but this gas is cooled and diluted before entering the bag house and when it leaves the stack it is only 1.04% CO. The level at other plants was claimed to be less than 1% CO. Although there is a reducing zone low in the furnace, the gases are burned to provide heat before leaving the furnace.

Tin smelting, done at only one plant in the U.S., produces about the same amount of CO as is produced in lead smelting. Copper smelting does not involve the use of coke and does not produce significant quantities of CO. Primary metal production site locations are shown in Figure 6.

METALLIC SILICON

All silicon produced in the U.S. is made in open-hooded electrical resistance furnaces, where essentially all of the CO produced is burned at the surface of the melt. Silica and coke are charged to the furnace. Stoking is required to break up the surface crust and to allow the gases to escape.

FIGURE 6. Geographical Distribution of Primary Metals Production Sites

This access requirement for stoking and charging requires open-hooded furnaces; it is unlikely that any way can be found to enclose the furnace and recover the wasted CO unless these requirements are met.

U.S. silicon producers are listed in Table 20. Production sites are shown in Figure 7.

SILICON CARBIDE (CARBORUNDUM)

Silicon carbide is used as an abrasive and as a component of high strength and chemical resistant articles.⁽¹⁷⁴⁾ It is made by the reaction between quartz sand and carbon in an electrothermic furnace. The sand (silicon dioxide) is 98 to 99.5% pure; the carbon consists of anthracite, coke, pitch, or petroleum coke. The reactions involved are:

TABLE 20. U.S. Silicon Producers

Company	Location	Plant Size, MW	Capacity for Si, 1000 tons/yr
Union Carbide	Alloy, WV	48	37
National Metallurgical Kawecki - Berylco Ind. Inc.	Springfield, OR	175	14
Hanna Nickel Smelting Hanna Mining Co.	Rock Island, WA	--	--
Interlake Corp.	Beverly, OH	--	--
Alabama Metallurgical Co., Inc.	Selma, AL	34	25
Reynolds Metals Co. (Chemicals Division)	Sheffield, AL	--	--
Dow Corning Corp.	Hemlock, MI	--	--

FIGURE 7. Geographical Distribution of Silicon and Silicon Carbide Production

It can be seen from the reaction that two molecules of CO are produced for every one molecule of silicon carbide (equivalent to 1.4 ton CO/ton SiC).

The furnace is charged in batch fashion, and heated electrically for 36 hr, before being allowed to cool for 24 hr. The process is claimed to be 50% energy-efficient, with a conversion efficiency of 70 to 80%.⁽¹⁷⁵⁾

Contacts with industry representatives determined that nearly all of the CO produced in this process burns in air at the surface, due to the extremely high reaction temperature. Actual off-gas compositions could not be provided, except to indicate that the CO content is "extremely low." Published data on CO concentrations at the surface of the furnace put the level at less than 0.5% CO.⁽¹⁷⁴⁾ Hence, the prospect for CO recovery from silicon carbide furnaces must be considered poor.

ELEMENTAL PHOSPHORUS

Elemental phosphorus is produced in the U.S. entirely by the electrothermic reduction of phosphate rock with carbon in the form of coke. Phosphate rock is primarily apatite and fluorapatite, $\text{Ca}_3(\text{PO}_4)_2$ and $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, but also contains a variety of other minerals such as silica, clays, iron, limestone and carbonaceous matter.

In this process the charge is heated by an electric arc in an essentially air-tight furnace to high temperatures which assure the reaction of the carbon with the oxygen component of the calcium phosphate mineral in the ore.^(176,177) At these temperatures the elemental phosphorus is produced in gaseous form and is carried from the furnace along with co-produced CO, entrained dust, hydrogen sulfide, carbonyl sulfide, phosphine and nitrogen. The calcium and silica, as well as most other minerals, are discharged as a molten slag, although one modification would generate recoverable ferrophosphorus, CO, calcium sulfide, and elemental phosphorus together.^(178,179)

The reactions which take place for either apatite or fluorapatite are considered to be:

Several side reactions result in the formation of ferrophosphorus alloy, volatile fluorine compounds, such as SiF_4 , and other gases, such as hydrogen sulfide and phosphine. However, with either of the principal reactions shown above the ratio of the phosphorus and CO products is the same, 2.5 moles of CO per mole of phosphorus--or on a weight basis, for every ton of phosphorus produced, two and a quarter (actually 2.26) tons of CO are obtained. Variations in mineral contents such as iron, silica, limestone and naturally occurring carbon as well as special operating conditions cause some departure in the ratio from theoretical. However, most manufacturers responded that actual observed ratios were near theoretical and one volunteered that 2.3 tons of CO were obtained per ton of phosphorus produced.

Though it was not possible to obtain detailed production figures, Table 21 gives data from reference and trade publications^(180,181) to assess the national production of phosphorus. Phosphorus production sites are shown in Figure 8. There have been reports of a major future expansion of capacity at the FMC plant at Pocatello, Idaho.

In these plants the CO, which is evolved in very concentrated form (98%), is to a large extent used as a convenient fuel in calcining, sintering, nodulizing and drying the ore to prepare feed for the furnaces. Thus, this otherwise nearly ideal CO resource must be regarded as unavailable except for some excess smaller amounts which are flared. However, if economic incentives were apparent, the fuel requirements could be as well provided by alternatives such as coal. In some cases, however, rather significant additions to the fuel, feed and combustion facilities may need to be justified. The continued escalation of natural gas prices suggests a more favorable basis for the

TABLE 21. U.S. Phosphorus Producers^(180,181)

Company	Location	Phosphorus Capacity Short Tons/yr	Estimated Annual Carbon Monoxide Production, tons/yr
FMC	Pocatello, ID	145,000	326,000
Monsanto	Columbia, TN	135,000	305,000
	Soda Springs, ID	95,000	215,000
Occidental (Hooker)	Columbia, TN	60,000	137,000
Stauffer	Mt. Pleasant, TN	45,000	102,000
	Silver Bow, MT	42,000	93,000
	Tarpon Springs, FL	23,000	52,000
ElectroPhos	Pierce, FL	22,000	50,000
Mobil	Nichols, FL	5,000	11,000
TOTAL		572,000	1,291,000

Shutdown, idle, or standby plants:

TVA	Muscle Shoals, AL	34,000
Mobil	Mt. Pleasant, TN	24,000
Baker	Georgetown, ID	21,000

consideration of an alternative, more highly valued use of available CO. Although CO, because of its significantly lower volumetric heat value in comparison with natural gas, inhibits its consideration for pipeline delivery over great distances, some favorable geographic situations do exist for its most convenient use as a chemical feed material. For example, by the conventional "shift conversion" process CO is readily and rather simply used to produce hydrogen:

Thus, CO could totally displace natural gas when employed for hydrogen production in ammonia manufacture. The J. R. Simplot Co. has a 110,000 tons/yr ammonia plant close to the FMC phosphorus plant at Pocatello, ID. This latter plant produces more than enough CO to produce hydrogen for the entire ammonia

FIGURE 8. Geographical Distribution of Elemental Phosphorus Production

production of Simplot. A similar situation exists between the Monsanto phosphorus plant at Soda Springs, ID, and the nearby ammonia plant of Beker Industries, and possibly between ammonia producers in the Tampa, FL, area and three phosphorus producers nearby. Alternatively, in the Pacific Northwest at least, the CO could be used to produce methanol for which a very large market exists in the plywood adhesives industry (about 200,000 tons/yr).

At an estimated 80% overall conversion efficiency, 1 ton of CO should yield one-third of a ton (650 lb) of anhydrous ammonia, or three-tenths of a ton (600 lb) of methanol.

CALCIUM CARBIDE

There are four commercial producers of calcium carbide with production at the five plant sites shown at Figure 9. Three of these plants operate with a hooded-type electrical resistance furnace equipped with Soderberg self-baking electrodes. These three furnaces produce an off-gas stream of 60 to 72% CO. The other two plants have open-topped furnaces which allow the CO to burn to CO₂ at the surface of the melt. Table 22 lists production of CaC₂ and CO at the plants presently active in the U.S.

Attempts to use the CO produced in this process have been sporadic at best. Patents describing the use of by-product CO as fuel were granted in 1896⁽¹⁸²⁾ and 1913.⁽¹⁸³⁾ Calcium carbide processes have been proposed in which the simultaneous production of producer gas,⁽¹⁸⁴⁾ hydrogen,⁽¹⁸⁵⁾ and phosphorus⁽¹⁸⁶⁾ was claimed. Calcium carbide production using carbon derived from natural gas has also been proposed.⁽¹⁸⁷⁾ In the past one plant used

FIGURE 9. Geographical Distribution of Calcium Carbide Production

TABLE 22. U.S. Production of Calcium Carbide

<u>Company</u>	<u>Location</u>	<u>Furnace Type</u>	<u>Plant Capacity</u>	<u>Potential Annual Carbon Monoxide Production</u>
Airco, Inc.	Louisville, KY	Semi-Sealed	50 MWe 150,000 tons/yr	56,000 tons
Midwest Carbide Corp.	Keokuk, IA	Semit-Sealed	13 MWe 30,000 tons/yr	13,000 tons
Gulf/Chemetron	Pryor, OK	Open Hood	20 MWe 50,000 tons/yr	
Pacific Carbide and Alloys Co.	Portland, OR	Open Hood	28,000 tons/yr	
Union Carbide Corp.	Ashtabula, OH	Semi-Sealed	228,000 tons/yr	

their waste CO for 70% of the underfiring power to recover CaO from the Ca(OH)_2 produced by making acetylene from the carbide. This process later became uneconomical and was discontinued. Others have studied CO utilization by recycling the gas to fire lime kilns. Use of CO in this type of cycle was estimated at 20 to 30% of the total available. Doubts were expressed about the utility of using the off-gas stream for a continuous-type of process due to the intermittency of furnace operation. A furnace shut-down rate of four times a day was considered a distinct possibility.

Present plans at one plant call for recycling the off-gas to fire a coke-drying oven. This sytem would use only 25 to 35% of the CO and the rest would be flared. One plant representative expressed hope that a use for CO by-product gas could be found because they have a large new furnace which could be hooded and put to work as a CO producer.

Almost all of the calcium carbide produced in the U.S. today is used to make acetylene for welding gas; none of the acetylene appears to be used as a chemical feedstock. A future use which may well be of value to the carbide industry is in the metallurgical field. Calcium carbide can be used in iron and steel furnaces to remove sulfur as CaS in the slag. This would allow the use of high sulfur cokes without negative effects on the metal purity or atmospheric quality.

CARBON BLACK

Carbon black is formed of amorphous carbon, used principally as an additive to rubber. It is produced by three processes, all involving incomplete combustion and/or pyrolysis of hydrocarbon feedstocks, using air and thus generating various quantities of CO.

Over 95% of U.S. production of carbon black is by the furnace process, a continuous process in which a high temperature vortex is generated by complete combustion of refinery tail gas or natural gas in air. A mist of preheated aromatic hydrocarbon heavy oil (decant oil, the bottom stream from a crude oil catalytic converter) is sprayed into the center of this high temperature zone (at 1350 to 1650°C) causing incomplete oxidation of the oil and the formation of carbon particles in about 35 to 65% yield (depending on the grade of carbon black being produced). The gases are saturated with water and cooled to 250°C before entering the bag house for carbon collection. The other process in use involves a thermal cracking of natural gas which produces no CO. A third process (the channel process) is still used at one plant but is obsolete. Both of the latter processes may soon be obsolete due to pressures on the natural gas supply.

The rate of production of CO varies with the grade of carbon black. Also, the industry has suffered from oil and gas shortages, and some plants have been run at reduced capacity or in one case have been closed down temporarily. Thus, the carbon black and CO production figures given below are only approximate.

There are presently eight companies in the industry, with 29 plants producing furnace black. These are shown in Figure 10 and listed in Table 23. It was determined that approximately 1.2 lb of CO are produced for each 1 lb of carbon black. The composition of the off-gas is variable, but typical values are CO (6 to 9%), water (45 to 50%), nitrogen (30 to 35%), carbon dioxide (2 to 3%), hydrogen (5 to 10%), and traces of acetylene and methane. To dispose of the waste CO, several plants burn the tail gas with injected natural gas (a double waste!). However, most plants just exhaust the off-gases, although some off-gas sensible heat content is recovered by passing it through heat exchangers. The chemical heat value of the gas is not recovered.

FIGURE 10. Geographical Distribution of Furnace Carbon Black Production

There is one expired patent which describes a modified method for the production both of carbon black and producer gas, then using the producer gas for making hydrocarbons by the Fischer-Tropsch method or for making methanol.⁽¹⁸⁸⁾ The furnace off-gas from the process had the composition: hydrogen (46.8%), CO (28.5%), water (16.6%), and small amounts of carbon dioxide, methane, acetylene, and nitrogen.

There is thus a good prospect both for recovery and use of the presently produced off-gas and for future conservation techniques involving some modifications to the existing processes.

Using sources different from those listed in Table 23, a state-by-state list of carbon black capacity and CO off-gas quantities was compiled (Table 24).

TABLE 23. U.S. Production of Carbon Black

By Company:

<u>Company</u>	<u>Locations</u>	<u>Carbon Black Capacity</u>
Ashland Oil Inc.	Aransas Pass, TX (F)	75 ^(a)
	Belpre, OH (F)	50
	Iberia, LA (F)	120
	Mojave, CA (F)	32
	Shamrock, TX (F)	55
Cabot Corp.	Big Spring, TX (F)	120
	Franklin, LA (F)	105
	Pampa, TX (F)	26
	Villa Platte, LA (F)	121
	Waverly, WV (F)	81
Cities Service Co.	Conroe, TX (F)	50
	El Dorado, AR (F)	40
	Eola, LA (F)	32
	Mojave, CA (F)	30
	Moundsville, WV (F)	75
	North Bend, LA (F)	75
	Seagraves, TX (F)	48
Thermatomic Carbon Commercial Solvents Corp.	Ulysses, KS (F)	25
	Sterlington, LA (T)	65
Continental Carbon Co.	Bakersfield, CA (F)	38
	Phenix City, AL (F)	On Standby
	Ponca City, OK (F)	68
	Sunray, TX (F)	47
	Westlake, LA (F)	60
J.M. Huber Corp.	Baytown, TX (F)	125
	Borger, TX (F, T)	62
Phillips Petroleum Co.	Borger, TX (F)	144
	Orange, TX (F)	48
	Toledo, OH (F)	40
Sid Richardson Carbon Co.	Addis, LA (F)	38
	Big Spring, TX (F)	68
TOTAL		1963

(a) Thousands of tons/yr.

(F) = Furnace.

(T) = Thermal (produces no CO).

TABLE 24. Carbon Black and Carbon Monoxide Potential in the U.S.

Region	Carbon Black Capacity (a)	Number of Plants	Carbon Monoxide Production (a)(b)
Texas	870	12	1040
Louisiana	550	7	660
California	100	3	120
Ohio/W. Virginia	250	4	295
Arkansas/Kansas/ Oklahoma	130	3	160
TOTALS	1900	29	2275

(a) Thousand of short tons/yr.

(b) Based on 1.2 lb CO/lb C produced.

TITANIUM DIOXIDE

Titanium dioxide is prepared commercially by the sulfuric acid digestion of ilmenite (approximately 50% TiO_2), and by the reductive chlorination of rutile (95% TiO_2).⁽¹⁸⁹⁾ Other processes involving the direct reduction of ilmenite with CO⁽¹⁹⁰⁾ and reductive chlorination using hydrogen chloride instead of chlorine⁽¹⁹¹⁾ have been proposed, but are not used. All of the processes require either a calcination or an oxidation of the intermediate (titanyl sulfate or titanium tetrachloride).

Reductive chlorination of rutile is the only commercially important method of making titanium dioxide which also generates large quantities of CO. In this process, rutile is heated with coke and chlorine:

The crude titanium tetrachloride vapors contain ferric chloride, silicon tetrachloride, phosgene, carbon monoxide, and chlorine impurities.⁽¹⁹²⁾ Ferric chloride is precipitated by washing with liquid titanium tetrachloride which is recycled. The gas stream is then cooled and the non-condensable

gases vented. The $TiCl_4$ is separated after distillation of $SiCl_4$ and other chloride impurities and is then oxidized in a burner supplied with air or oxygen, producing pigment grade titanium dioxide.

Very little process information was supplied by titanium dioxide producers. The off-gas was quoted as being in the range of 5 to 30% CO. This corresponds to 0.3 to 1.0 tons of CO per 4 tons of TiO_2 . There is extensive gas purification in this process, to recycle chlorine and minimize toxic emissions.

Table 25 lists the U.S. producers of titanium dioxide (by the reductive chlorination process only, or about 70% of the total), and Figure 11 shows their geographical distribution.

TABLE 25. Titanium Dioxide Production by the Chloride Process

Owner	Location	TiO_2 Capacity, thousands of tons/yr	Carbon Monoxide Production ^(a)
American Cyanamid Co. ^(b)	Savannah, GA	40	12
E.I. duPont deNemours & Co. ^(c)	Antioch, CA	30	2
	Edge Moore, DE	167	10
	New Johnsonville, TN	228	13
Gulf Western Indust. New Jersey Zinc Co.	Ashtabula, OH	9	7
Kerr-McGee Corp.	Hamilton, MS	50	22
SCM Corp., Glidden-Durkee ^(b)	Ashtabula, OH	27	12
	Baltimore, MD	29	13

(a) Estimated CO production in thousands of tons/yr.

(b) License from Kerr-McGee Corp.

(c) 130,000 tons/yr of TiO_2 will be produced at a new plant to be built for duPont at DeLisle, MS, to start operation in 1979.⁽¹⁹³⁾

FIGURE 11. Geographical Distribution of Titanium Dioxide Production

PETROLEUM REFINING

The sources of CO in a petroleum refinery include catalyst regenerators, coking operations, flares, boilers, and process heaters. Only moving-bed catalyst regenerators and fluid cokers produce significant amounts of CO. The total CO production from U.S. petroleum refineries shown in Figure 12 is estimated to be 14 million tons/yr (see Table 26) of which over 90% comes from fluid catalytic cracker (FCC) regenerators.

The reactor of an FCC unit is a large vertical cylinder in which powdered catalyst is kept in a fluidized state by the flow of vaporized feedstock. The regenerator is a similar vessel located near the reactor so that catalyst circulates between the reactor and regenerator continuously. The cracking reaction results in coke formation on the catalyst, and this coke is burned off

in the regenerator. In most FCC regenerators conditions are maintained which minimize oxidation of CO to CO₂ to prevent after-burning in the top of the regenerator. After-burning causes temperature runaways which damage the catalyst. The composition of flue gas from a typical FCC regenerator is shown in Table 27.

TABLE 26a. U.S. Petroleum Refinery Operations
(January 1, 1975)

	<u>Number of Plants</u>	<u>Throughput</u>
Crude Capacity	259	15,500,000 BPOD ^(a)
Catalytic Cracking Capacity (Fresh Feed, no Recycle)	144	4,676,000 BPOD
FCC	121	(4,360,000 BPOD)
TCC	20	(266,000 BPOD)
HCC	3	(50,000 BPOD)
Fluid Coking		135,000 BPOD

a. Barrels per operating day.

TABLE 26b. Carbon Monoxide Production from Refinery
Catalytic Processes

	<u>Emission Factor lb CO/1000 EBL</u>	<u>Total Carbon Monoxide Production^(a) Tons/yr</u>
FCC	16,500	11,800,000
TCC	3,800	166,000
HCC	3,800	30,000
Fluid Cokers	30,000	665,000
TOTAL		12,661,000

a. Based on capacities in Table 26a and a 90% operating factor.

TABLE 27. Typical Composition of Flue Gas
from FCC Regenerator

CO	8%
CO ₂	8%
H ₂ O	8%
O ₂	1%
N ₂	75%
SO _x	200-2000 ppm
NO _x	<u>100-600 ppm</u>
TOTAL	100%

FIGURE 12. Geographical Distribution of Petroleum Refineries
with Catalytic Processes that Produce Carbon Monoxide

In 70 to 80% of U.S. refineries with FCC units the regenerator flue gas is burned in a CO boiler to recover the heating value of the CO and to satisfy air pollution requirements. In the other refineries the flue gas is flared.

Until recently all FCC regenerators were operated as described above. However, advancements in regenerator technology have made it possible to burn all the CO in the regenerator itself, thus eliminating the need for a CO-fired boiler. This new technology, referred to as high temperature regeneration (HTR), not only recovers the heating value of the CO but provides other operating benefits such as increased conversion and lower coke production. Any new FCC units will almost certainly be designed for HTR, and many existing units without CO boilers should find HTR economically attractive. For existing FCC units with CO boilers it is not yet clear whether the modifications necessary for HTR can be justified solely on the operating benefits obtained.

The other processes which produce significant amounts of CO are all similar to an FCC unit and include Thermoform Catalytic Cracking (TCC) units, Houdriform Catalytic Cracking (HCC) units, and fluid cokers. The major difference is that TCC and HCC units utilize bead or pelleted catalysts and in fluid coking the coke itself is the fluidized solid. The flue gases are similar in composition to FCC flue gases.

ORGANIC CHEMICALS

Many organic chemicals are made by processes which involve partial oxidation. Partial oxidation of any organic chemical has the potential of generating some CO. One example is Dow Chemical's acetylene off-gas COSORB purification plant, where by-product CO is used to make phosgene for toluene diisocyanate production. Another is an ammonia-generating unit based on waste CO from a stationary diesel engine.⁽¹⁹⁴⁾

We were unable to identify any large-scale sources of high concentration waste CO in the organic chemical industry, partly because industry is reluctant to discuss sources of CO, and partly because organic chemical producers are already well aware of the potential of waste CO as an intermediate. A

number of potential and likely sources are listed in Table 28. For the most part, even if a substantial proportion of the total yield is in the form of CO, there would be insufficient quantities to merit isolation. However, substances such as adipic acid and maleic anhydride are exceptions. Large-scale sources of CO may exist within some industries; but without the cooperation of industrial representatives, and published data, it is difficult to assess the potential for CO recovery.

TABLE 28. Organic Chemicals as Potential Sources of By-Product Carbon Monoxide

Organic Chemical Synthesis Processes which may serve as By-Product Sources of CO

Acetaldehyde by oxidation of ethylene
 Acetaldehyde by oxidation of ethanol
 Acetic acid by oxidation of acetaldehyde
 Acetic anhydride by oxidation of acetaldehyde
 Acetone by oxidation of isopropanol
 Acrylic acid by oxidation of propylene
 Acrylonitrile by oxidation of propylene and ammonia
 Adipic acid by oxidation of cyclohexane
 Ethylene oxide by oxidation of ethylene
 Fumaric acid and Maleic anhydride by oxidation of benzene
 Methanol production from CO and H₂
 (purge gas contains CO and H₂)
 Terephthalic-phthalic anhydride by oxidation of xylene
 Vinyl acetate by oxidation of ethylene and acetic acid
 Phthalic acid by oxidation of naphthalene^(a)
 Formaldehyde by oxidation of methanol^(a)

(a) Faith Keyes and Clark's Industrial Chemicals, 4th Edition, Cowenheim & Moran.

OTHER SOURCES OF CARBON MONOXIDE

Barium Sulfide

Barium sulfide is produced by roasting barium sulfate with coke. The concentration of CO is about 5% at the top of the kiln, but this hot gas is allowed to oxidize in air and the CO₂ is recycled to precipitate BaCO₃. The total production of all barium chemicals was only 62,000 short tons in 1973.

Calcium Sulfide

Calcium sulfide is produced by the reduction of gypsum (calcium sulfate) with coke: (195,196)

Although a large volume of CO is produced relative to the calcium sulfide, much of it is burned, and in any case the overall quantities involved are small. Calcium sulfide is used in the tanning and specialty paint industries.

Boron Trichloride

Phosgene is produced as a by-product of boric acid chlorination to boron trichloride. The phosgene is converted to CO. (197)

Oxychlorination

The combined reaction of ethylene, (198) propylene, (199) or petroleum coke (200) with hydrogen chloride and air is used in industry to produce vinyl chloride, allyl chloride, and other chlorinated organics, respectively. Carbon monoxide is produced in small amounts as a by-product. In the oxychlorination of ethylene to dichloroethene by HCl and air, CO formed by oxidation of ethylene was shown to be converted to CO₂. (201)

Carbon Monoxide in Process Purge Gas

A small proportion of the synthesis gas used to make methanol is purged to the atmosphere or burned, because continued recycling of the synthesis gas builds up minor atmospheric components (the inert gases, principally argon).

Similar purging is to be anticipated in the new process for acetic acid production by carbonylation of methanol, and in future processes for producing synthetic higher fatty acids by carbonylation of olefins.⁽²⁰²⁾

Although the proportion of gas purged is small (approximately 5%), its CO concentration is high (up to 30%). Given the large production volumes for methanol and acetic acid, the total tonnage will be large. Detailed figures for the CO wasted in these processes are not known, but purging could be an important source of waste CO.

Carbon Monoxide in Ammonia Synthesis Gas

Ammonia synthesis gas is made by a combination of natural gas steam-reforming and oxidation of the carbon in natural gas. Both produce hydrogen, together with CO in the oxidation step.

The synthesis gas is adjusted to the composition required by stoichiometry ($3\text{H}_2:\text{N}_2$) for ammonia synthesis. Carbon monoxide interferes with the catalyst for ammonia synthesis, and has to be removed. In newer plants this is done by methanation (conversion to methane with hydrogen), but in older plants, the ammonia synthesis gas is purified using the copper liquor scrubbing method. This generates a side stream of relatively pure CO, which is normally used for fuel, although its use for conversion to sodium formate has been recommended.⁽²⁰³⁾

Paper Pulp

Two basic processes used for making paper pulp are the Kraft process and the sulfite process; both involve recovery of inorganic salts by combustion of paper pulping residual liquors. The Kraft process is presently operated with efficient burning in both the lime kilns and the sodium sulfide recovery boilers.⁽²⁰⁴⁾ The off-gas contains less than 1% of CO. In the past, to lower operating costs, the boilers were run over capacity. This led to inefficient oxidation above the reduction zone and 2 to 3% of CO in the off-gas. With today's tighter pollution controls this is no longer allowed to happen.

There are five variations of the older sulfite process. Only the processes using magnesium or sodium-based liquors involve inorganic salt recovery, and much of the incentive for this is pollution abatement. There is one report of magnesium oxide recovery from a sulfite mill in which the off-gas contained CO (14%),⁽²⁰⁵⁾ and a U.S. patent exists on the subject of sulfite liquor gasification.⁽²⁰⁶⁾ However, as only 11 pulping plants in the U.S. today use the sodium or magnesium-based pulping process, and these are gradually being supplanted by the more efficient Kraft process, there is little prospect for CO recovery in them. In most cases, the off-gas CO content is too low for practical recovery.

Charcoal

Generation of wood charcoal by destructive distillation (pyrolysis) was once a major U.S. industry. By-products from the charcoal preparation included methanol, acetic acid, and off-gases containing up to 27% of CO,^(207,208) together with useful amounts of methane and hydrogen.

Today, approximately 685,000 tons/yr of charcoal are produced in the U.S. In the newer multiple-hearth continuous-retort the gases are captured, and in some cases the condensable tars are recovered. Up to 1/3 of the off-gas is used as fuel to dry briquettes and the remainder is flared. Analysis showed about 12% of CO in this off-gas, but no flow rates were available. Total tonnages could not, therefore, be calculated.

In the older Missouri kiln process (resembling the original beehive coke oven), the smoke is vented to a flare, and no attempt is made to recover the gaseous by-products.

Other Pyrolysis Processes

Rising fuel costs have prompted some municipalities to examine using their trash as a fuel source. Various processes under development range from direct pyrolysis to high-pressure liquid phase gaseous reduction.

Incineration without product recovery has been used for many years. All forms of pyrolysis of carbonaceous waste yield CO as a by-product, both the natural organic portions of the waste (wood, etc.), as noted above, and the newer synthetic plastics. The formation of CO in plastics pyrolysis has been noted for rubber,⁽²⁰⁹⁾ PVC,⁽²¹⁰⁾ polyurethanes,⁽²¹¹⁾ and plexiglas.⁽²¹²⁾ Since such processes not only provide boiler fuel but also remove large volumes of trash from municipal dumps, it is to be expected that this procedure will gain rapidly in importance. By-product CO recovery could be advantageous in the future, although the source is negligible today.

Miscellaneous Sources of Carbon Monoxide

There are many sources of dilute CO in industry. Apart from the obvious stack gas CO source, some of these are: the metal decorating process,⁽²¹³⁾ with large volumes of off gases containing up to 0.07% CO; foundry sand binders based on formaldehyde resins;⁽²¹⁴⁾ aluminum surface treatments;⁽²¹⁵⁾ and acetone cyanhydrin purification off-gases.⁽²¹⁶⁾ These are mentioned merely to indicate the diversity of CO sources. There are undoubtedly many more low-grade sources of CO, and high total tonnages of dilute gas wasted by venting to atmosphere. None of these are economically recoverable at present. As a rough guide, CO concentrations of less than 5% are not currently economically recoverable, although it is technically feasible to do so.

CONCENTRATION METHODS FOR CARBON MONOXIDE RECOVERY

COPPER-AMMONIUM PROCESSES AND VARIANTS

The copper-ammonium process is based on a discovery by LeBlanc⁽²¹⁷⁾ in 1850 that CO will be absorbed by solutions containing cuprous salts of weak acids. The phenomenon became the basis for the cuprammonium CO absorption technique still used worldwide in industry (e.g., 218, 219). Six thorough reviews of the process and its variants have been published.⁽²²⁰⁻²²⁵⁾ Many recent research articles have also dealt with various new techniques and problems of the process (for example, 48, 226-239), and detailed kinetic and mechanistic studies^(228,240-246,267-275) indicate that process development continues. However, the COSORB process may make the copper-ammonium absorption method obsolete.

The copper-ammonium process is illustrated diagrammatically in Figure 13. The basic reaction is:

Evidence for the above equation was obtained by isolation of the solid complex $\left[\text{Cu}(\text{NH}_3)_3\text{CO} \right] \text{Cl} \cdot \text{H}_2\text{O}$.⁽²³⁷⁾ Copper carbonyls per se are not involved, although they have been shown to exist at low temperatures.⁽²⁴⁷⁾ This change is reversed by heat in the desorption side of the cycle. Carbon dioxide is also absorbed to some extent by the ammonia, forming ammonium carbonate and ammonium bicarbonate. Again, this is reversed in the desorption step. Troublesome side reactions which have never been effectively circumvented are:

FIGURE 13. Copper-Ammonia Carbon Monoxide Absorption System

Equation (1) represents the loss of CO through its reduction of cupric ion (always present to some extent in the solution), while (2) shows the loss of cuprous ion by disproportionation to elemental copper and cupric ion. This is a major source of trouble in the cuprammonium process. To avoid copper metal precipitation, the cupric ion concentration has to be maintained. This is done by adding a small amount of oxygen to the gas stream, causing oxidation of cuprous ion to cupric ion (Equation 3).

Besides the strictly chemical problems of side reactions in the cuprous system, a physical problem is the system's dependence on the presence of ammonia, a volatile gas. Thus, in the desorption step, where the cuprous/ammonium/CO complex is decomposed by heat, some ammonia is always lost. The

loss of ammonia can be regulated to some extent by the weak acid anion used in the process. For instance, formate permits less ammonia loss than carbonate due to the relatively higher decomposition pressure of the carbonate, but this is self limiting: an ammonium salt with a low dissociation pressure will reduce ammonia loss, but will also reduce ammonia availability to the copper ions.

Despite these problems, the copper-ammonium process has been operated successfully for many years at a large number of plants. Although not optimal, it works. Table 29 gives typical operating data for a Tennessee Valley Authority copper-ammonia system.

TABLE 29. TVA Copper Liquor Scrubbing System

<u>Operating Variable</u>	<u>Value</u>	
	<u>Absorption</u>	<u>Desorption</u>
CO content of gas entering primary scrubber	2.8%	--
CO content of scrubbed gas	<5 ppm (secondary scrubber)	73.6% (leaving reflux)
Gas temperature entering primary scrubber	97°F	--
Gas temperature leaving desorption		11°F
Gas flow	8350 cfm	--
Gas pressure	1690 psig	0-1.5
Ammonia makeup	0.75 lb/min	--
Acetic acid makeup	1070 lb/month	--
Formic acid makeup	480 lb/month	--
Cu ⁺ concentration	87.4 g/l	--
Cu ⁺ /Cu ²⁺ ratio	4.03	--
Total solution volume	25,750 gal	

No plants built in the U.S. in the past 10 years use the copper liquor scrubbing system. Cryogenic processes (discussed later) have been used instead. A relatively recent modification of the copper liquor absorption system was built for town-gas purification at Winterthur, Switzerland in about 1961. Described as the Sulzer CO removal process,^(248,249) this process uses a solution of cuprous and magnesium chlorides to absorb CO from town-gas at atmospheric pressure and room temperature, and gives a product containing 95% CO by vacuum desorption at 30 torr. Although a considerable advantage is thus gained over conventional CO absorption in copper scrubbers, the changeover from town-gas to natural gas on the one hand, and the advent of the more efficient COSORB process on the other, will probably make this variant obsolete also.

Some form of cuprous ion appears necessary for CO absorption. In other applications of cuprous complexes in solution for removal of CO from gas mixtures, copper/ethanolamine complexes have been used to separate CO from tetrafluoroethylene,⁽²⁵⁰⁾ and mixtures of CO₂ and CO have been separated using the heat of reaction of potassium carbonate with CO₂ to power the desorption cycle of the copper liquor scrubbers.⁽²⁵⁰⁾ In a reversal of the CO-recovery process, the formation of the cuprous carbonyl chloride complex has been used to win copper from bornite and chalcopyrite by leaching the ores with hydrochloric acid in the presence of CO,⁽²⁵²⁾ and the CO-mediated reduction of metal amines has also been applied to metal formation.⁽²⁵³⁾ Solid cuprous chloride has been complexed with butadiene in a fluidized bed to recover butadiene by complexation in a fashion similar to the recovery of CO.⁽²⁵⁴⁾

There is still potential for using the copper chloride/ammonia process to recover CO and other complexible materials. The copper liquor process itself, however, suffers from a number of disadvantages not easily remedied: the precipitation of copper metal, loss of ammonia from the desorption step, and occasional instability of the $\text{Cu}^+/\text{Cu}^{2+}$ ratio. One other difficulty not previously mentioned is that the waste water from copper liquor plants contains highly toxic copper complexes in suspension.⁽²⁵⁵⁾ Tight pollution controls represent a more recent difficulty for the copper liquor process.

THE COSORB PROCESS

The disadvantages of the copper/ammonia process for CO recovery have been known for many years, and there have been many attempts to identify alternatives that do not suffer from these disadvantages. Promising results were obtained by replacing the water solvent with a nonaqueous solvent, such as propionitrile.⁽²⁵⁶⁾ Unfortunately, propionitrile is volatile under the conditions used for the CO desorption, and is considerably more toxic than ammonia. This problem was apparently overcome in a 1971 patent assigned to the Monsanto Chemical Co., in which the copper complex is the tetrafluoroborate or hexafluorophosphate, and the nonaqueous solvent was toluene or other aromatic hydrocarbon, or an olefinic hydrocarbon.⁽²⁵⁷⁾ However, precipitation of the complex formed with CO apparently caused mechanical problems with this system.

The COSORB process is the most recent advance in nonaqueous copper systems. The solvent is toluene and the copper complex is cuprous tetrachloroaluminate.⁽²⁵⁸⁻²⁶³⁾ The process was developed for Tenneco Chemicals, Inc. and is now commercially available.⁽²⁶⁴⁻²⁶⁶⁾ A feasibility study for large-scale separation of CO from producer gas has been completed.⁽²⁶⁷⁾ Discussions with the originators of the process, and data from the patent literature^(268,269) yielded the following information:

The process was operated on a pilot plant scale for almost 2 years without major difficulty, and is now being operated commercially by the Dow Chemical Co.⁽²⁷⁰⁻²⁷⁶⁾ at Freeport, Texas. The demonstration plant operated on acetylene synthesis off-gas containing CO (24.77%), hydrogen (71.53%), and small amounts of nitrogen and methane, and had a capacity of 212,000 lb/yr. The commercial unit operates at 75 million lb/yr capacity. It is anticipated that a major application of the COSORB process will be the purification of CO from coal gasification, for chemicals manufacture. The product CO can have a purity of 99.83% (see Table 30 for gas composition data). The copper solution replacement time is anticipated to be greater than 5 years, using a 30% CO feedstock. The spent solution is regenerated by adding anhydrous

TABLE 30. Comparison of Carbon Monoxide Recovery Processes^(a)

Feed ^(b)		Gas Component					
		CO Product			H ₂ Product		
Gas	Vol%	COSORB	Cu Liquor	Cryogenic	COSORB	Cu Liquor	Cryogenic
CO	24.8	99.8	98.5	99.4	0.17	0.16	1.9
H ₂	71.5	0.12	1.4	0.15	94.9	94.9	98.1
CH ₄	3.6	0.05	0.07	0.2	4.8	4.8	0.01
N ₂	0.07	10 ppm	7 ppm	00.27	0.09	0.09	0.01
CO ₂	50 ppm	0	50 ppm	0	0.1	0	0
Recovery %		99.5	96.9	87.3	99.9	99.5	96.7

(a) After Reference 260.

(b) Total 6.54×10^5 scf/hr.

ammonia, filtering off the precipitate of cuprous chloride, and dissolving again in aluminum chloride and toluene.⁽²⁷⁷⁾ The purified CO from the Dow plant will be used to make toluene diisocyanate for polyurethane manufacture, and for acrylate synthesis. It can also be used in separating Group IB (gold, silver, copper) halides⁽²⁷⁷⁾ from their mixtures with other halides, by a reversal of the COSORB reaction.

The COSORB process's major disadvantage is that the feed gas must be water-free to 1 ppm. This is accomplished by passing the feed through alumina or molecular sieves at 50 to 100 psi pressure. The advantages of COSORB over the conventional copper liquor process are:

- tolerant to oxygen to the explosive limit
- will operate in mild steel equipment
- operates at 20°C (absorber) and less than 111°C (desorber)
- does not precipitate copper or require Cu⁺/Cu²⁺ ratio balancing
- lower capital cost
- product purity of 99+%.

These claims for the COSORB process obviously indicate a considerable advantage over the copper liquor process and even cryogenic separation. Estimated cost for CO made from methanol purge gas by the COSORB process is 2¢/lb⁽²⁷⁷⁾ at a 2000 m³/hr plant capacity (however, see the section on economics for additional economic data).

LOW-TEMPERATURE SEPARATION PROCESSES

Separation of CO from gas mixtures by liquefaction or by washing with a liquified gas has been performed for many years. There are a number of reviews of the process,⁽²⁷⁸⁻²⁸⁴⁾ plus articles dealing with the recovery of CO and/or hydrogen by this method from reformed natural gas,^(285,286) coke-oven gas,^(287,288) ammonia synthesis gas⁽²⁸⁹⁾ and so on. Kinetic studies dealing with gas mixture gas-liquid equilibria^(290,291) are also available. There have been many variations and improvements reported in the patent literature (for example, 292-301), although the basic process remains a strictly physical separation applicable to gas mixtures generally, provided that the components differ sufficiently in their boiling points.

Cryogenic separation is condensation of a gas mixture to liquid form, pumping off any uncondensed components (usually hydrogen) and fractional distillation of the remainder to separate the required component. The greater the difference between the boiling point of the required component (CO) and the other components, the greater the efficiency of the separation. Unfortunately, CO boils at -190°C, nitrogen at -196°C, and oxygen at -183°C, very small differences. Since these three gases are usually associated in mixtures, cryogenic separation is of less value in this case than for many other separations (CO and hydrogen, for instance). Despite this, cryogenic separation of CO has in recent years supplanted the copper liquor process, since it is simpler and more economical to operate, although in some instances it is cheaper to remove CO entirely through methanation⁽³⁰²⁾ rather than recover it.

ALTERNATIVE CONCENTRATION METHODS

The three processes outlined above for CO concentration and recovery all have some disadvantages. Copper/ammonia absorption plants have so many that they are probably obsolete. Cryogenic recovery plants require that the gases be thoroughly dried, and cooled to -200°C . Most waste gases are hot, and the CO recovered for use in almost any chemical reaction has to be heated to up to 400°C before use. The cooling step is thus wasteful of energy. The COSORB process requires thorough drying and removal of H_2S , ammonia and SO_2 before passing through the absorber solution. Thus, improved CO concentration processes are needed.

Union Oil Hypersorption Process

Developed originally in England and Germany during 1937-44⁽³⁰³⁾ this cannot be considered to be a new process; however, the principle on which it is based allows for further development. In essence, a cooled gas stream passes over a cooled moving bed of activated and purified charcoal at -50°C , where some gas components are selectively adsorbed. The charcoal is then removed from contact with the gas stream and warmed to desorb the entrapped gas. The process of selective adsorption is technically applicable to any gas mixture and using any adsorbent (e.g., 304-309) although the Hypersorption process applied only to activated carbon.

The first plant was built in 1947 for the Dow Chemical Co.⁽³¹⁰⁾ by Union Oil and Foster-Wheeler Corp., for ethylene recovery. Data on this plant are shown in Table 31. A patent on a similar process⁽³¹¹⁾ assigned to Phillips Petroleum Co. in 1951, deals with the separation of H_2/CO from nitrogen on charcoal and silica, and the use of an iron-group impregnated adsorbent has also been claimed.⁽³¹²⁾

Membrane Separation Processes

Passage of a mixture of CO and other gases through a membrane will often partially separate CO by differences in the physical parameters of the gaseous molecules.⁽³¹³⁻³¹⁶⁾ The principle is now under commercial development in the case of CO/H_2 separation. Recent advances in hollow fiber

TABLE 31. Hypersorption Plant Data for
Synthesis Gas Separation(a)

Component	Feed Gas, vol%	Unadsorbed Gas, vol%	Desorbed Gas, vol%
H ₂	52.5	59.0	0
N ₂	4.5	5.1	0
CO	29.1	32.7	0
CH ₄	1.0	1.1	0.2
CO ₂	12.5	2.1	96.2

(a) After Reference 310.

membrane module preparation have made possible the construction of membrane separators with very high surface area/volume ratios, formerly a major problem. McCandless⁽³¹⁷⁾ has described experiments in which common plastics (Dacron, Mylar, Nylon, etc.) have been used to separate a 1:1 volume/volume mixture of CO and hydrogen, with a single pass separation factor of up to 115.

These membranes depend on a passive separation (the membrane does not combine chemically with the gas components). General Electric is reported to be developing active membranes which will pass SO₂ and O₂ selectively by means of a chemical reaction of the component gas with the membrane material itself, excluding all gases which do not so react, and they have also reported a chemical membrane system for separation of nitric oxide.⁽³¹⁸⁾

Membrane separation technology is a new field which has considerable potential for the future. It does not require toxic chemicals, high pressures, complex control equipment, or low temperatures. Depending on the particular application, membranes may not require pre-purification of the gas mixture from contaminants such as H₂S or water. However, it is unlikely that membranes can be made to operate at temperatures much above 150°C unless they can be made without the use of organic polymers. For separation of CO from

hydrogen, a membrane process may be advantageous. However, for separation of CO, oxygen, and nitrogen, an active system may be required, since these gases are notoriously difficult to separate from one another by a passive system.

Organometallic Carbonyl Complex Formation

Until a few years ago, very few chemical systems were known which would react reversibly with gaseous CO. They were restricted to the Cu^+ ion systems (copper/ammonia), and silver ion,^(319,320) although the formation of nickel carbonyl was considered.⁽³²¹⁾ The rapid development of organometallic chemistry, and the large amount of research done on ways to fix the chemically similar molecule, nitrogen, have changed the picture considerably. Now many carbonyl complexes are known, some of them capable of reacting with CO, N_2 , and O_2 at room temperature and pressure. Complete coverage of the voluminous literature on this subject is not possible here; instead, examples will be given to illustrate the principle involved.

None of these examples are directly applicable to CO concentration in industry since the critical requirements of reversibility and stability are not met, but such compounds are possible future alternatives to chemical concentration of CO by cryogenic or conventional absorption methods.

The first example is dicyclopentadienyltetramethylenetitanium⁽³²²⁾ (Figure 14a) prepared from dicyclopentadienyltitanium dichloride and 1,4-dilithiobutane. The compound is only stable below -40°C , but will react with CO at -78°C and atmospheric pressure to form the carbonyl insertion product. On warming to room temperature, this decomposes to cyclopentanone and unidentified titanium compounds. This example was chosen because it demonstrates the high reactivity of some organometallic compounds toward CO. One titanium compound has been isolated⁽³²³⁾ which reacts reversibly with hydrogen at -80°C , indicating that reversible reaction of similar compounds with CO is more than a possibility. In fact, a molybdenum complex has been shown to absorb CO at 25°C and to release it from the complex on purging with nitrogen at 111°C ⁽³²⁴⁾ (Figure 14b). The potential of this reaction

for industrial application has apparently not been explored, although the use of molybdenum complexes for the reversible fixation of atmospheric nitrogen (iso-electronic with CO) has been extensively studied (e.g., 325). In fact, there is a concerted effort in progress to "fix" atmospheric nitrogen under mild conditions, react this to form ammonia, and regenerate this catalyst for more nitrogen "fixing." This process would replace current ammonia synthesis technology if it could be made practicable, and would mimic the bacterial nitrogen fixation which occurs on the roots of legumes. Nitrogen and CO are very similar in their reactions, and it is highly likely that success in the nitrogen fixation field would also indicate success in CO fixation. Incidentally, many of the compounds which react under mild conditions with nitrogen and CO also react with oxygen and ethylene.

A further example is that of Tanaka and Tanaka;⁽³²⁶⁾ the reaction of bis(triphenylphosphino)nickel(II)bis(diethylselenocarbamate) with CO to produce bis(triphenylphosphino)nickel(0) dicarbonyl (Figure 14c). The carbonylation reaction occurs in 40 minutes to 3 hours (depending on the route) at atmospheric pressure and room temperature. The carbonyl decomposes at 200°C. This reaction scheme could be modified to be reversible, and is thus a candidate for a CO separation process.

There is thus a great potential in the metal carbonyl reaction area of chemistry for selective low temperature and pressure gas purification and concentration methods to be developed in the future.

Other Organometallic Compounds

Although there are many possibilities in the literature for ways of absorbing CO (e.g., 327-333), one of the most promising of early development into a workable system is the polyoxime-copper chelate complex recently reported by Kim and Takizawa.⁽³³⁴⁻³³⁶⁾ The reversible absorption of CO by this material has been demonstrated; a system with a long enough life to satisfy industrial designers remains to be accomplished. The material is made by copolymerizing ethylene and CO (1:2 ratio) to a molecular weight of about 4000, adding a copper salt after converting the C=O groups to the oxime

FIGURE 14. Organometallic Compounds with Potential as Carbon Monoxide Absorption Agents

(addition of hydroxylamine will do this), and reacting the copper-polyoxime chelate complex with hydrazine. The derivative was found capable of absorbing 3.2 liters of oxygen in water or 0.8 liters of CO in methanol per gram atom of copper, at 20°C in 6 hours. The rate of uptake was greater for CO than for oxygen. Heating at 70° reversed the addition. On cooling, the same amount of CO was taken up again. Also, on transferring to water the additional product of the polymer with CO, a further 0.8 liters of CO/g-atom Cu were taken up, making a total of 1.6 l CO/g-atom Cu. The number of

reversions possible, the rate of decomposition of the polymer, and other essential data were not given, so it is not yet possible to compare this system directly with the conventional copper/ammonia or COSORB processes. However, on a strictly chemical basis, it is promising. The iron complex is even more active than the copper complex.

CARBON MONOXIDE PURIFICATION

After concentration of CO from waste gases, small amounts of specific pollutants in the CO must usually be removed. The actual degree of purity of the CO and the nature of the contaminants which must be removed will vary according to the end use of the CO--for instance, hydrogen sulfide and iron carbonyl must be removed from methanol synthesis gas, since otherwise it would poison the catalyst.⁽³³⁷⁻³³⁹⁾

Unfortunately, the literature abounds with references to the removal of CO from gases, rather than the removal of other gases from CO. This is understandable since CO is commonly thought of as a pollutant rather than as a valuable chemical feedstock. Theoretically, such CO-removal processes could serve in either sense, since they achieve a separation of CO and other gas mixture components. Practically, most removal processes destroy the CO by oxidation with a catalyst and air,⁽³⁴⁰⁻³⁵⁴⁾ or employ methanation^(355,356) shift conversion to hydrogen,⁽³⁵⁷⁻³⁵⁹⁾ redox reactions with sulfur and nitrogen oxides,⁽³⁶⁰⁻³⁷⁰⁾ chemical reaction with metal powder⁽³⁴³⁾ or hydrogen sulfide,⁽³⁷¹⁾ reduction with sulfates⁽³⁷²⁾ or thiosulfates,⁽³⁷³⁾ or direct combustion.⁽³⁷⁴⁾

It is unfortunate that there is no current research into reversible absorption of CO from large-volume dilute sources, such as tunnel air or stack gases, since this could provide significant amounts of CO. The only reversible application identified used cuprous chloride suspensions⁽³⁷⁵⁻³⁷⁷⁾ to remove CO from tunnel air, but this is a new application of an old process.

Actual purification of CO by removal of contaminants, other than by COSORB and similar processes, has been the subject of very little patent activity, although one article deals with methods of preparing pure CO for reaction

with uranium.⁽³⁷⁸⁾ Basic compounds such as ammonia have been removed from CO by passage through sulfonated ion exchange resins impregnated with nickel salts.⁽³⁷⁹⁾ Removing traces of hydrogen from CO was the subject of a specialized process involving hydride formation between hydrogen and LaNi_5 .⁽³⁸⁰⁾ This was a reversible reaction. An irreversible removal of hydrogen (and sulfur compounds) from CO has been described, in which oxidation over a catalyst was used to obtain pure CO.⁽³⁸¹⁾ Hydrogen sulfide separation from CO would be effected by charcoal or molecular sieves according to conventional practice, although another method has been proposed.⁽³⁸²⁾ In other specialized purification processes, CO was freed of traces of phosphorus by selective oxidation,⁽³⁸³⁾ and from iron carbonyl by cation exchange resin.⁽³⁸⁴⁾ Equilibrium data on the N_2 -P-CO System is available.⁽³⁸⁵⁾ There is a single report of aluminum production off-gas purification by scrubbing.⁽³⁸⁶⁾

In major chemical processes using CO (e.g., ammonia production), the former practice was to purify and concentrate the CO in a copper liquid scrubbing system.⁽³⁸⁷⁾ In ammonia synthesis gas purification this procedure has been largely replaced by CO reduction to the inert gas methane. There is thus no recovery of the residual CO from the shift reaction to hydrogen in ammonia synthesis, and the methane is eventually burned with the purge gas. In the case of methanol synthesis, purge gas can be recycled through a small "piggyback" reactor to produce more methanol.⁽³⁸⁸⁾

Thus, although industrial CO is undoubtedly purified before conversion, the exact procedure varies so much from process to process that few details have been published, and in most cases the procedure may be proprietary.

PRODUCTION OF MAJOR INDUSTRIAL CHEMICALS BASED ON CARBON MONOXIDE

Carbon monoxide generation, isolation, and purification have been dealt with in preceding sections of the report. Now the various chemical processes in which CO is used, either directly or after conversion into hydrogen by the water gas shift reaction, will be reviewed. Since development of processes requiring CO as a feedstock is by no means complete, a subsequent section deals with potential, as opposed to actual processes, by which CO may be converted into a wide variety of chemicals.

Some of the many uses for CO in the chemical industry are shown in Figure 15. This figure includes processes in current use, as well as several which may be developed in the near future.

The organic chemicals discussed in the following section are classified into methanol and derivatives (formaldehyde, acetic acid, etc.) oxo-chemicals, ammonia and derivatives (urea and acrylonitrile), and phosgene and derivatives (isocyanates and urethanes).

METHANOL

Methanol is synthesized by the reaction of a stoichiometric mixture of CO and hydrogen.

Cu-based catalyst

60% yield without recycle

Heated methanol must be supplied to initiate the reaction, but once started it continues spontaneously with the evolution of 24.62 kcal/mole of heat. The methanol is condensed under operating pressure, and the residual gases recycled (with some purge to eliminate any buildup of inert contaminants). Two variants of the process are used; the older one uses pressures of 200 to 330 atm

FIGURE 15. Major Chemical Production from a Carbon Monoxide Base

at 300°C with a zinc/chromium oxide catalyst, and the newer one uses a copper-containing catalyst and operates at 50 to 100 atm and 250 to 270°C. The process yields methanol of 99%+ purity; small amounts of dimethyl ether and higher alcohols are the major impurities.

The chief outlet of methanol is in formaldehyde synthesis by oxidation (Table 32). Although it is theoretically possible to generate formaldehyde directly by the reaction:

so many by-products are formed that the indirect method of manufacture through methanol is used almost exclusively.

Methanol production is expected to increase by 6 to 10% through 1979, to 1400 million gal/yr in 1979. Sites of production are given in Figure 16, and are listed in Table 33.

TABLE 32. Uses of Methanol^(a)

Formaldehyde synthesis	45
Methyl halides	4
Methylamines	4
Methyl methacrylate	4
Dimethyl terephthalate	7
Solvent uses	10
Other	<u>26</u>
	100

(a) Data in this and following tables are adapted from Chem. Marketing Reporter, Stanford Res. Inst. Directory of Chemical Producers, 1976, and personal communications.

TABLE 33. Manufacturers and Plant Sites for Methanol Production

Manufacturer	Location ^(a)	Capacity ^(b)
Air Products	Pensacola, FL	160
Borden, Inc.	Geismar, LA	510
Celanese Corp.	Bishop, TX	510
Celanese Corp.	Clear Lake, TX	740
Commercial Solvents Corp. (International Minerals and Chemicals Corporation)	Sterlington, LA	160
E. I. duPont deNemours & Co., Inc.	Beaumont, TX	640
E. I. duPont deNemours & Co., Inc.	Orange, TX	370
Georgia Pacific	Plaquemine, LA	320
Hercules	Plaquemine, LA	
Hercules	Hercules, CA	345
Monsanto	Texas City, TX	320
Rohm and Haas	Deer Park, TX	70
Tenneco	Houston, TX	<u>260</u>
TOTAL		4405

(a) Other companies, particularly DuPont, are expected to increase their capacities in the near future.

(b) Thousands of tons/yr.

FORMALDEHYDE

Formaldehyde is made either by catalytic vapor-phase oxidation of methanol or by a combination oxidation-dehydrogenation process. Formaldehyde and the unreacted methanol in the product gases are absorbed in water and separated by distillation in either process.

Generally, air and methanol are mixed mechanically or by maintaining the methanol at a constant level and temperature in the vaporizer, through which air is drawn. The alcohol-air mixture contains 30 to 50% methanol. Residual alcohol spray is vaporized in a preheater.

The reactor contains a silver or copper gauze catalyst. The reaction over these catalysts is a combination of dehydrogenation and oxidation, the former being responsible for high yields, whereas the latter supplies heat and aids in keeping the catalyst active. The best metal oxide catalyst is a mixture of molybdenum, iron, or vanadium oxides. The reaction over this type of catalyst is mainly one of oxidation and requires a large excess of air, at a catalyst temperature of 450 to 600°C and a contact time of about 0.01 sec.

Separation of methanol and formaldehyde is accomplished by alternate scrubbing and cooling; the gases then pass to a final scrubber fed with cold water and are vented to the atmosphere. These exit gases contain 19 to 22% hydrogen and 74 to 75% nitrogen. The gases also contain between 4 and 5% carbon dioxide, together with traces of CO, oxygen, and methane.

The combined condensate and scrubber liquor from the main column (containing formaldehyde, water, and approximately 15% unreacted methanol) are fed into a fractionating column, where 37% formaldehyde plus the desired amount of methanol stabilizer is removed from the bottom and excess methanol is removed from the top and returned to the vaporizer. Overall yields are 85 to 90% by weight based on the methanol charged.

Essentially all formaldehyde is produced from methanol. Of the two processes starting with methanol, the one using the oxide catalyst gives higher yields but is also more expensive to operate. The process is particularly suitable for large plants.

The cost of methanol-oxidation plants in the 50,000 tons to 200,000 tons/yr capacity range is about \$1 to 2.5 million.

Formaldehyde is used mainly in making synthetic resins. The current annual growth rate for urea-formaldehydes is about 6%, for melamine-formaldehydes 5%, and for acetals 10%.

Formaldehyde is no longer used for the production of ethylene glycol. A major new use is the manufacture of tetrahydrofuran, 3,4-butanediol, and polytetramethylene ether glycol, from formaldehyde. Another substantial new use for formaldehyde is the manufacture of methylenedianiline (MDA) from the reaction with aniline. MDA is used as an additive in urethane rubbers and for the manufacture of methylene diphenylisocyanate (MDI), a urethane feed stock. Uses of formaldehyde are listed in Table 34. Manufacturers and plant sites are listed in Table 35, and are illustrated in Figure 17.

TABLE 34. Uses of Formaldehyde

Urea-formaldehyde	} resins	30%
Phenol-formaldehyde		24%
Acetal		9%
Melamine-formaldehyde		4%
Pentaerythritol		6%
Hexamethylenetetramine		6%
Tetrahydrofuran		3%
Chelating Agents		3%
Acetylene derivatives		3%
Other		<u>12%</u>
		100%

TABLE 35. Manufacturers and Plant Site for Formaldehyde Production

Manufacturer	Location	Capacity ^(a)
Allied Chemical Corp.	South Point, OH	155
Borden, Inc.	Bainbridge, NY; Demopolis, AL; Diboll, TX; Fayetteville, NC; Louisville, KY; Sheboygan, WI; Fremont, CA; Kent, WA; LaGrande, OR; Missoula, MT; Springfield, OR	662
Celanese Corp.	Bishop, TX; Newark, NY; Rock Hills, SC	867
Chembond Corp. (Skelly Oil Co.)	Springfield, OR; Winnfield, LA	105
Commercial Solvents Corp.	Sterlington, LA; Seiple, PA	48
E. I. duPont deNemours & Co., Inc.	Belle, WV; La Porte, TX; Healing Springs, NC; Linden, NJ Toledo, OH	700
GAF Corp.	Calvert City, KY	50
Georgia Pacific Corp.	Albany, OR; Columbus, OH; Coos Bay, OR; Crossett, AR; Taylorsville, MS; Vienna, GA; Russellville, SC	500
Gulf Oil Corp.	Vicksburg, MS	23
Hercules, Inc.	Louisiana, MO; Wilmington, NC	135
Hooker Chemical Corp.	North Tonawanda, NY	68
Monsanto Company	Addyston, OH; Chocolate Bayou, TX Eugene, OR; Springfield, MA	345
Pacific Resins and Chemicals	Eugene, OR	48
Reichhold Chemicals, Inc.	Hampton, SC; Houston, TX; Kansas City, KS; Mancure, NC; Tacoma, WA; Tuscaloosa, AL; White City, OR, Malvern, AR	425
Rohm and Haas Company	Philadelphia, PA	13

TABLE 35. (Cont'd)

Manufacturer	Location	Capacity ^(a)
Tenneco, Inc.	Fords, NJ; Garfield, NJ	143
Union Carbide Corp.	Bound Brook, NJ	60
Wright Chemical Corp.	Acme, NC	40
TOTAL		4387

(a) Thousands of short tons/yr.

FIGURE 17. Geographical Distribution of Formaldehyde Production

ACETIC ACID

Acetic acid is produced by three major routes, including oxidation of acetaldehyde from butane oxidation, and methanol carbonylation. Methanol carbonylation, a recent innovation, seems highly competitive with other processes and is likely to be of considerably greater relative importance in the future. Because of its relevance to the present study, methanol carbonylation will be the only acetic acid production process described here.

The reaction is:

The yield is 99%+ based on methanol.

There are high pressure (BASF) and low pressure (Monsanto) processes, differing mainly in the catalyst. The reaction occurs in the liquid phase at 175°C and 1000 psi in the presence of a rhodium and iodine-based catalyst, and at 250°C and 7500 psi with a cobalt and iodine-based catalyst (represented as RhI_2 and CoI_2 above, although this is not the complete structure): In the Monsanto process, methanol and CO are passed through a continuous reactor system with a homogeneous catalyst containing rhodium and iodine. The acetic acid withdrawn from the reactor system is purified by conventional distillation. Small amounts of light ends from the reactor system combined with the light ends column overhead are scrubbed and recycled.

The crude acetic acid is dried and purified. The overhead from the product column is fed to the finishing column, where acetic acid of high purity is recovered. Overhead and bottoms from the finishing column, as well as the wet acid taken as overhead from the drying column, are recycled to the reaction system. The acetic acid product has a purity of 99.9% with a yield of 99.5% based on the methanol feed.

Almost half of the acetic acid produced is used in the manufacture of vinyl acetate, and nearly a quarter in the manufacture of cellulose acetate via acetic anhydride. Acetic acid is also used in the manufacture of

terephthalic acid (TPA) which is used in the manufacture of polyester fibers. Continuing vinyl acetate growth, with a strong polyester market, assures a growing demand for acetic acid. Uses for acetic acid are listed in Table 36; manufacturers and plant sites in Table 37.

TABLE 36. Uses of Acetic Acid

Vinyl acetate	40.0%
Cellulose acetate	23.0%
Acetic esters	12.0%
TPA/DMT	10.0%
Textile processing	3.0%
Chloroacetic acid	2.5%
Other	<u>9.5%</u>
	100.0%

TABLE 37. Manufacturers and Plant Sites for Acetic Acid Production

<u>Manufacturer</u>	<u>Location</u>	<u>Capacity</u> ^(a)
Borden, Inc.	Geismar, LA	55
Celanese Corp.	Bay City, TX;	55
	Clear Lake, TX	200
	Pampa, TX	275
FMC Corp.	Bayport, TX	20
Monsanto Company	Texas City, TX	200
Publicker Industries, Inc.	Philadelphia, PA	40
Sonoco Products Company	Hartsville, SC	?
Tennessee Eastman Company	Kingsport, TN	200
Union Carbide Corp.	Taft, LA;	45
	Texas City, TX;	50 ^(b)
	Brownsville, TX	<u>320</u>
TOTAL		1410

(a) Thousands of short tons/yr.

(b) On standby. Not included in total.

More than 90% of the domestic output is currently derived from either the liquid-phase oxidation of butane or from the oxidation of acetaldehyde, although two producers have recently developed improved methods for the manufacture of acetic acid via the CO-methanol process, making this competitive.

The advantages of the Monsanto process are the high yield of acetic acid, the reduction in capital and operating cost for the reaction and purification systems as compared with other processes, and the absence of significant amounts of by-products even in the presence of hydrogen.

ACETIC ANHYDRIDE

Two processes to produce acetic anhydride are based on acetaldehyde and on acetic acid. Only the second process is important today.

In the process based on acetic acid, vapors of glacial acetic acid containing 0.2 to 0.3% triethylphosphate are passed into a tubular reactor heated to 700 to 800°C under reduced pressure (200 torr). As the reaction gases leave the converter, ammonia gas is injected into the stream to prevent reversion of the ketene in the product.

The reactor exit vapors containing acetic anhydride, acetic acid, ketene, and water are fed to condensers where weak acetic acid (30%) is condensed before it can react with the ketene. The uncondensed ketene is absorbed in acetic acid to give acetic anhydride (90% purity), which is then fractionated.

Ketene may also be prepared from acetone according to the reaction

In this process acetone vapors are passed through a void chrome-iron tube, at 650 to 670°C. The contact time is about 0.25 to 5 seconds. Unreacted acetone is condensed and recycled and ketene is absorbed in glacial acetic acid to give acetic anhydride. Yields based on acetone are about 80 to 95%, with a conversion per pass of 15 to 25%.

Acetic anhydride is made in greatest quantity by its chief users, cellulose acetate manufacturers, or by integrated organic chemical manufacturers who make a variety of related compounds. Manufacturers and uses for acetic anhydride are listed in Table 38 and 39, respectively.

TABLE 38. Manufacturers and Plant Sites for Acetic Anhydride Production

<u>Manufacturer</u>	<u>Location</u>	<u>Capacity</u> ^(a)
Celanese Corporation	Pampa, TX;	150
	Rockhill, SC;	125
	Harrison, VA	125
FMC Corp.	Meadsville, PA	30
Tennessee Eastman Co.	Kingsport, TN	300
Union Carbide Corp.	Brownsville, TX;	100
	Texas City, TX	<u>on standby</u>
TOTAL		830

(a) Thousands of short tons/yr

TABLE 39. Uses of Acetic Anhydride

Cellulose esters (including cellulose acetate, acetate butyrate, and acetate propionate)	95%
Aspirin	1%
Other	<u>4%</u>
	100%

Future acetic anhydride manufacture is expected to be closely related to the demand for cellulose acetate, and to be governed by gains or losses of the latter in the textile and plastics fields.

VINYL ACETATE

Two processes used today for the production of vinyl acetate are the vapor phase reaction between acetylene and acetic acid in the presence of zinc acetate catalyst, and the vapor phase ethylene process.

In the acetylene/acetic acid reaction, acetylene is scrubbed of hydrogen sulfide and phosphorus compounds, and mixed in slight excess with vaporized acetic acid. The reaction is exothermic over the 10% zinc acetate catalyst and the reactor is cooled by circulating oil to maintain the reactor temperature at 175 to 200°C. The reactor effluent is condensed and acetylene, methyl acetylene, propadiene, and other light ends are removed. The acetylene must be repurified before recycling.

Vinyl acetate is then distilled overhead in a vinyl acetate column and acetic acid is separated from heavy ends in a recovery column for recycle. The conversion per pass is 60 to 70%, with an overall yield of 97 to 99% based on acetic acid.

The second process involves the reaction of ethylene with acetic acid. Superheated acetic acid vapor is mixed with ethylene and oxygen and reacted over a palladium catalyst. Since the reaction is strongly exothermic, steam is produced and used for the distillation. The reactor is kept at 175 to 200°C and 70 to 140 psi. The reactor mixture is cooled and condensed, and gas-liquid phase separation is effected under full pressure. The gas is recycled to the reactor after washing and passage through a desorber to eliminate carbon dioxide.

The liquid products are released into a second separator, where the dissolved gas is released and then separated by distillation. Water, acetaldehyde, and a small amount of polymer are the impurities. The acetic acid is recycled to the reactor. The yield is 91 to 95% vinyl acetate with a conversion per pass of 15 to 30%, based on acetic acid.

Vinyl acetate is used entirely for polymer manufacture. Both dominant end-use markets for vinyl acetate--adhesives and coatings--have expanded rapidly. Uses of vinyl acetate are used in Table 40; manufacturers and plant sites are listed in Table 41 and shown geographically in Figure 18.

TABLE 40. Uses of Vinyl Acetate

Polyvinyl acetate	55%
Polyvinyl alcohol	15%
Polyvinyl chloride copolymers	7%
Ethylene-vinyl acetate copolymers	4%
Other	<u>19%</u>
Total	100%

TABLE 41. Manufacturers and Plant Sites for Vinyl Acetate

<u>Company</u>	<u>Location</u>	<u>Annual Capacity</u> (a)	<u>Raw Material</u>
Borden, Inc.	Geismar, LA	80	Acetylene
Celanese Corp.	Bay City, TX	150	Ethylene
Celanese Corp.	Clear Lake, TX	175	Ethylene
E. I. duPont de Nemours & Company, Inc.	LaPorte, TX	175	Ethylene
National Starch and Chemical Corp.	Long Mott, TX	30	Acetylene
Union Carbide Corp.	Texas City, TX	175	Ethylene
United States Industrial Chemicals	Deer Park, TX	<u>187</u>	Ethylene
		972	

(a) Thousands of short tons/yr.

FIGURE 18. Geographical Distribution of Acetic Acid and Acetyl Group Products Manufacture

OXO AND REPPE CHEMICALS

Several industrial chemicals are made by similar reactions. For ease in classification and discussion, they are all included under one heading. Reaction of CO with hydrogen alone will produce methanol (and some hydrocarbons). If ethylene or another olefin is included, aldehydes and alcohols are formed by the Oxo reaction. Reaction of CO, hydrogen, and an acetylene (usually acetylene itself) will produce unsaturated acids or esters (the Reppe reaction). This reaction is used to make acrylic acid and acrylate esters. The scheme of reactions for these processes is shown in Figure 19. (This figure is intended to give general information and is not intended to be a comprehensive summary of the industry.)

1. ACRYLATE ESTERS (REPPE REACTION)

2. OXO CHEMICALS

(CO AND HYDROGEN USE POINTS ARE MARKED)

FIGURE 19. Carbon Monoxide Use for Acrylate, Alcohol, and Aldehyde Production Via the Modified Reppe and the Oxo Processes

Acrylic Acid and Acrylate Esters

Acrylates are produced by a modified Reppe process involving acetylene, an alcohol, and CO in the presence of an acid. In commercial practice 80% of the CO comes from the gas and 20% from the nickel carbonyl catalyst. The process is continuous; nickel chloride is recovered and converted back to nickel carbonyl.

The reaction is initiated by reacting nickel carbonyl with acetylene and ethyl alcohol in the presence of hydrochloric acid, with an acrylate initiator. Once the stoichiometric process is established, the catalytic process is superimposed by feeding in CO, acetylene, ethyl alcohol, water and hydrochloric acid so that CO becomes a primary reactant and nickel carbonyl acts as a catalyst and a secondary source for CO. The reaction occurs at 30-50°C and 1-2 atm pressure. The reaction liquid is washed with nickel chloride to remove alcohol and nickel salts and to salt out the ethyl acrylate. The crude monomer is removed from the top of the extractor and is washed to neutralize acids. It is then purified by distillation under reduced pressure. The yield is approximately 80%.

In a modification of this process, acrylic acid is made by an improved catalytic method and is then esterified separately. Lower acrylates, (methyl and ethyl) are prepared by the modified Reppe technique, while higher acrylates are produced through transesterification or by direct esterification with acrylic acid.

The most recent process for acrylates is based on the oxidation of propylene in a continuous 2-stage vapor-phase oxidation reaction. Over 20% of United States acrylate capacity is via the propylene route.

Acrylates have experienced approximately 20% annual growth rate over the last 10 years. Future growth is expected to be about 15%/yr

through 1977, with a drop to 12% in 1978. United States demand for acrylate esters is expected to rise from an estimated 600 million lb in 1975 to over 1175 million lb in 1978.

The most commercially significant acrylates are methyl, ethyl, butyl, and 2-ethylhexyl acrylate, with ethyl acrylate accounting for over 60% of production in 1972, followed by butyl acrylate (27%) and 2-ethylhexyl acrylate (10%). Direct oxidation of propylene to acrylic acid, followed by esterification is expected to be the most economical synthesis route for the future, unless petroleum prices rise steeply again.

The major markets for acrylates are in surface coatings and textiles. Uses of acrylates are listed in Table 42; manufacturers and plant sites are given in Table 43.

TABLE 42. Uses of Acrylates

Coatings	45%
Textiles	25%
Fibers	5%
Polishes	5%
Paper	5%
Leather	3%
Exports	6%
Other	6%
	<u>100%</u>

TABLE 43. Manufacturers and Plant Sites for Acrylate Production

<u>Company</u>	<u>Location</u>	<u>Process</u>	<u>Capacity</u> ^(a)
Celanese Corp.	Pampa, TX; Clear Lake, TX	Sohio technology	155
Dow Badische Co.	Freeport, TX	Reppe	20
Rohm and Haas Co.	Deer Park, TX	Reppe	200
Union Carbide Corp.	Taft, LA	Propylene oxidation and esterification	<u>125</u>
Total			500

(a) Thousands of short tons/yr.

FIGURE 20. Sites of Acrylate Production in the U.S.

Oxo Chemicals

Alcohols and aldehydes of chain lengths C_3 to C_{20} may be made by the Oxo process in which olefins are reacted with CO and hydrogen to form aldehydes (of one carbon atom more per molecule than the reacting olefin), which are then hydrogenated to the corresponding alcohols. The Oxo reaction occurs in the presence of a cobalt-containing catalyst.

The feed olefin, synthesis gas, and an oil-soluble cobalt salt, such as cobalt naphthenate are reacted at 160 to 175°C and 1500 to 4000 psi. The cobalt naphthenate is converted to cobalt hydrocarbonyl, which is the active form of the catalyst.

The raw aldehyde leaving the reactor is freed of cobalt by lowering the pressure of the reactor effluent to 20 psi and adding steam. The cobalt is removed from solution as either metallic cobalt or the oxide.

The cobalt-free product is then hydrogenated at 150°C and 100 atm pressure in the presence of a suitable catalyst (nickel or copper chromite). Usually a small amount of water (1 to 10%) is added to suppress ether formation.

The hydrogenation products are separated by distillation, giving an overall yield of about 70% alcohols, based on the olefin feed.

Isooctyl, decyl, and tridecyl alcohols are made by the Oxo process, with smaller quantities of higher alcohols up to C_{20} also being produced. Large quantities of propylene are converted to a 4:1 mixture of n-butyraldehyde and isobutyraldehyde by the Oxo process. n-Butyl alcohol and 2-ethylhexanol are made respectively by hydrogenation of n-butyraldehyde, or by the aldolization, dehydration, and hydrogenation of n-butyraldehyde at 150°C and 150 atm in the presence of a nickel catalyst. A less important product is isobutanol which is produced by hydrogenating isobutyraldehyde.

n-Butanol, or n-butyl alcohol, was first produced on a large scale during World War I as a by-product of acetone produced by the fermentation of cornstarch.

Today, however, only two fermentation plants still operate; they account for approximately 6% of production. Almost two-thirds of n-butyl alcohol is produced from butyraldehyde via the Oxo process.

Isobutyl alcohol competes to some extent with n-butyl alcohol for solvent uses and amine resins.

2-ethylhexanol is the best-known of the synthetic higher aliphatic alcohols, with a 1973 production of over 220 thousand tons. It is produced by aldol condensation of butyraldehyde, which can be derived from propylene via the Oxo process or from acetaldehyde via ethylene. The Oxo process is the preferred route.

The major use of 2-ethylhexanol is in the manufacture of plasticizers, such as di-2-ethylhexylphthalate which is used in vinyl chloride resins. Its use may decline in the future because of replacement by linear alcohols.

2-ethylhexanol is also used to manufacture 2-ethylhexyl acrylate, an intermediate used in adhesive and surface-coating applications. Minor uses of 2-ethylhexanol include its use as a solvent, in the manufacture of herbicides, as a dispersing and wetting agent, and as a cosolvent for nitrocellulose.

Isodecyl alcohol is used in the manufacture of diisodecyl phthalate and diisodecyl adipate and other esters used as plasticizers for plastics, particularly polyvinyl chloride. Straight-chain higher alcohols with 11 or more carbon atoms are now favored in the detergent industry since they are biodegradable. The uses of these products are tabulated in Table 44. Table 45 lists the manufacturers and plant sites in the U.S.; Figure 21 shows these graphically.

TABLE 44. Uses of Higher Alcohols

Higher Alcohols

Water-soluble nonionics	49%
Alcohol sulfates	6%
Ether sulfates	12%
Viscosity-index improvers	6%
Tridecyl alcohol (Oxo)	15%
Other	<u>12%</u>
	100%

n-Butanol

Solvent	25%
<u>n</u> -Butyl acetate	10%
Glycol ethers and esters	15%
Plasticizers	10%
Amine resins	15%
Butyl acrylate and butyl methacrylate	15%
Other	<u>10%</u>
	100%

Isobutanol

Solvent	25%
Lubricating oil additive	25%
Amide resins	10%
Other	<u>40%</u>
	100%

2-Ethylhexanol

Plasticizers	80%
2-Ethylhexyl acrylate	10%
Other	<u>10%</u>
	100%

TABLE 45. Manufacturers and Plant Sites for Oxo Chemicals Production

Company	Location	Capacity ^(a)		
		Higher Alcohols	C ₄ Alcohols Aldehydes	2-Ethyl-hexanol
Continental Oil Co.	Westlake, LA	40	90	
Dow Badische Co.	Freeport, TX		80	20
Eastman Chem. Products, Incorporated	Longview, TX		90	50
Exxon Chem. Co.	Baton Rouge, LA	100		
Getty Oil Co.	Delaware City, DE	20		
Monsanto Co.	Texas City, TX	110		
Oxochem Enterprise	Penvelas, PR		55	95
Shell Chemical Co.	Deer Park, TX		80	20
Union Carbide Co.	Geismar, LA	75		
	Penvelas, PR		45	25
	Seadrift, TX	15	30	15
	Texas City, TX	25	75	
U.S. Steel Chemicals Co.	Haverville, OH	45		
TOTAL		430	545	225

(a) Thousands of tons/yr (1976).

FIGURE 21. Geographical Distribution of Oxo Process Chemicals Production

AMMONIA

Nitrogen and hydrogen in a stoichiometric ratio are reacted catalytically at high temperatures and pressures to produce ammonia. Hydrogen is obtained almost entirely by steam reforming of natural gas according to the equation:

The natural gas is preheated, passed over a bauxite catalyst to remove the sulfur, and then steam reformed. By use of a nickel catalyst in the reformer, a 70% conversion of methane to CO and hydrogen is attained. The partially reformed gas is then led to a combustion furnace where sufficient air is added to give nitrogen and hydrogen concentrations in the 1:3 molar ratio required for best yields in the ammonia synthesis reaction. The combustion chamber also contains a nickel catalyst, so the reforming reaction is completed.

The gases are cooled to 425°C and then fed to a shift converter where CO is reduced to less than 1%, by the water gas reaction:

An alternative process for preparation and purification of ammonia synthesis gas is hydrocarbon partial oxidation. In the partial oxidation process air is liquefied and then separated into oxygen of 95% purity and nitrogen of 99.99% purity. The reforming and combustion chamber steps of the process described above are replaced by a partial oxidation unit using 95% oxygen and a large excess of natural gas. The effluent gases, chiefly CO and hydrogen, are quenched and processed through a shift converter and a monoethanolamine unit. The last traces of CO and any residual hydrocarbons are removed by washing with liquid nitrogen in a low-temperature wash tower.

The purified 1:3 nitrogen-hydrogen mixture is compressed to 130 to 650 atm, at 400 to 600°C, with an average of about 475°C. At the inlet to the reactor, recycled unconverted nitrogen and hydrogen are added to the fresh gas.

The catalyst for ammonia synthesis is iron oxide, promoted by addition of small amounts of aluminum, potassium, calcium, or magnesium oxides.

The iron oxide is reduced to iron in the catalyst chamber by the nitrogen-hydrogen mixture, leaving a porous iron containing promoters. The catalyst is ruined by contact with phosphorus, arsenic, and sulfur; CO greatly reduces its activity. See Appendix B for additional discussion of catalyst poisons.

The gases leaving the reactor are cooled (-10 to -20°C), to liquefy some of the ammonia. Part of the gas is purged (to prevent accumulation of diluents such as argon), and the purge gas is used for fuel. The remaining gas is recompressed and recycled. The conversion per pass is approximately 20 to 22% and the overall yield with recirculation is 85%.

In 1974, greater than 80% of the ammonia produced came from steam reforming of hydrocarbons: more than 65% of this was based on natural gas feedstock.

A small amount of ammonia is recovered from coke-oven operation principally as aqua ammonia. Ammonia production in terms of volume of production is the third largest chemical of any kind, exceeded only by sulfuric acid and oxygen. Uses of ammonia are listed in Table 46.

TABLE 46. Uses of Ammonia

Fertilizer and feeds	76%
Fiber and plastics intermediates	9%
Explosives	4%
Other	<u>11%</u>
	100%

Shortages and high prices of natural gas will cause new plants to consider other raw materials. Where natural gas becomes expensive compared to heavier hydrocarbons, a shift from reforming to partial oxidation processes will take place. Coal-based ammonia production can only be justified where the cost of the coal is very low, or where natural gas and imported oil or naphtha are not available.

The greatest change in ammonia technology of the late 1960s and early 1970s is a great increase in the capacity of individual plants. Early plants had capacities of as little as 20 tons/day, but such small units have been or are being shut down. Most new plants have capacities of at least 800 tons daily. Table 47 lists manufacturers and capacities in the U.S. Geographic locations are given later in Figure 22.

UREA

Urea is produced by the indirect dehydration of the intermediate, ammonium carbamate, formed by the high-pressure reaction of excess ammonia and carbon dioxide.

TABLE 47. Manufacturers and Plant Sites for Ammonia Production^(a)

Company	Location	Capacity ^(b)
Air Products and Chemicals, Inc.	New Orleans, LA Pensacola, FL	220 ^(c) 75
Allied Chemicals Corp. Specialty Chemicals Division	South Point, OH	340
Agricultural Department	Geismar, LA	340
Fibers Division	Omaha, NB	156
American Cyanamid Company Agricultural Division	New Orleans, LA	340
Industrial Chemicals and Plastics Division	New Orleans, LA	n.a.
Apache Powder Company	Benson, AZ	14
Baker Industrial Corp.	Carlsbad, NM Conda, ID	190 95
Borden Inc. Borden Chemical Division Petrochemicals	Geismar, LA	300
California Oil Purification Co.	Ventura, CA	54 ^(d)
CF Industrial, Inc.	Tyner, TN Donaldsonville, LA Fremont, NB Tunis, NC Terre Haute, IN	165 760 ^(e) 50 210 135
Coastal States Gas Corp. Colorado Interstate Corp., subsid. Wycon Chemical Company, subsid.	Cheyenne, WY	145
Columbia Nitrogen Corporation	Augusta, GA	140 ^(f)
Cominco American Inc. Camex, Inc., subsid.	Borger, TX	400
Cooperative Farm Chemicals Assoc.	Lawrence, KS	380
Diamond Shamrock Corp. Diamond Shamrock Oil and Gas Co.	Dumas, TX	160
Dow Chemical U.S.A.	Freeport, TX	115
E.I. duPont deNemours & Co., Inc. Biochemicals Department Elastomer Chemicals Department Plastics Products and Resins Dept.	Belle, WV Beaumont, TX Victoria, TX	340 340 100

TABLE 47. (Cont'd)

Company	Location	Capacity ^(b)
El Paso Natural Gas Company		
El Paso Products Company, subsid.	Odessa, TX	117
Enserch Corporation		
Nipak, Inc., subsid.	Kerens, TX	105
	Pryor, OK	101
Farmland Indust., Inc.	Dodge City, KS	230
	Enid, OK	412 ^(g)
	Fort Dodge, IA	215
	Hastings, NB	158
	Pollock, LA	412
Felmont Oil Corporation	Olean, NY	82
First Mississippi Corporation	Fort Madison, IA	320
	Donaldsonville, LA	
FMC Corporation		
Chemical Group		
Industrial Chemicals Division	South Charleston, WV	22
Gardinier, Inc.		
U.S. Phosphoric Products	Tampa, FL	133
Gardinier Big River, Inc.	Helena, AR	182
Georgia Nitrogen Inc.	Gordon, GA	35
Goodpasture, Inc.		
Western Ammonia Corp., subsid.	Dimmitt, TX	62
W. R. Grace and Company		
Agricultural Chemicals Group	Big Spring, TX	98
	Memphis, TN	331
Green Valley Chemicals Corp.	Creston, IA	35
Gulf + Western Indust., Inc.		
The New Jersey Zinc Co., Div.	Palmerton, PA	36
Hercules Inc.		
Synthetics Department	Hercules, CA	70
	Louisiana, MO	70
International Minerals & Chemicals Corp., Chemical Group		
Commerical Solvents Corp., subsid.	Sterlington, LA	340
Jupiter Chemical Company	Lake Charles, LA	56

TABLE 47. (Cont'd)

Company	Location	Capacity ^(b)
Kaiser Aluminum & Chemicals Corp. Kaiser Agricultural Chemicals Div.	Savannah, GA	150
Kearney Chemicals Inc.	Gramercy, LA	12
Mississippi Chemicals Corp.	Pascagoula, MS Yazoo City, MS	195 385
Mobil Oil Corporation Mobil Chemicals Co., Division Petrochemicals Division	Beaumont, TX	260
Monsanto Company Monsanto Agricultural Products Co.	Luling, LA	420
N-Ren Corporation Cherokee Nitrogen Division	Pryor, OK	83
High Plains Division	Plainview, TX	25
N-Ren Southwest, Inc., subsid.	Carlsbad, NM	66
Occidental Petroleum Corporation Hooker Chemicals Corporation, subsid. Hooker Chemicals and Plas- tics Corp., sub. Electrochemical and Specialty Chemicals Division	Tacoma, WA	25
Occidental Chemical Company, subsid. Jefferson Lake Sulphur Co., Div.	Taft, LA Plainview, TX	82 55
Western Division	Hanford, CA Lathrop, CA	40 195
Olin Corporation Agricultural Chemicals Division	Lake Charles, LA	476
Pennwalt Corporation Chemical Division	Portland, OR	10
Phillips Pacific Chemical Co.	Kennewick, WA	150
Phillips Petroleum Company Fertilizer Division	Beatrice, NB Pasadena, TX	210 228
PPG Indust., Inc. Chemical Division Industrial Chemicals Division	Natium, WV	33
Reichhold Chemicals Inc.	St. Helens, OR	90
Rohm and Haas Company Rohm and Haas Texas Inc., subsid.	Deer Park, TX	50

TABLE 47. (Cont'd)

Company	Location	Capacity ^(b)
St. Paul Ammonia Products, Inc.	East Dubuque, IL	225
J. R. Simplot Company Minerals and Chemicals Division	Pocatello, ID	54
Skelly Oil Company Hawkeye Chemicals Company, subsid.	Clinton, IA	140
Standard Oil Company of California	El Segundo, CA Richmond, CA	5 120
Chevron Chemicals Company, subsid. Ortho Division	Fort Madison, IA	95
Standard Oil Company (Kentucky), subsid.	Pascagoula, MS	475
Standard Oil Company (Indiana) Amoco Oil Company, subsid.	Texas City, TX	681
The Standard Oil Company (Ohio) Vistron Corporation, subsid. Chemicals Department	Lima, OH	440
Tenneco Inc. Tenneco Chemicals Inc. Organics and Polymers Division	Houston, TX	200
Tennessee Valley Authority	Muscle Shoals, AL	68
Terra Chemicals Internat'l., Inc.,	Port Neal, IA	204
Texas Sulfur Products Co.	Lake Charles, LA	60
Tipperary Corporation	Lovington, NM	99
Triad Chemicals	Donaldsonville, LA	350
Tyler Corporation Atlas Powder Company, subsid.	Joplin, MO	129
Union Oil Co. of California Collier Carbon and Chemicals Corp., Subsid.	Brea, CA Kenai, AK	270 520
United States Steel Corporation USS Agri-Chemicals Div.,	Cherokee, AL Chicago, IL Clairton, PA Decatur, GA Geneva, UT La Mirada, CA Lodi, NJ San Mateo, CA	175 n.a. 325 n.a. 70 n.a. n.a. n.a.

TABLE 47. (Cont'd)

Company	Location	Capacity ^(b)
Valley Nitrogen Producers, Inc.	El Centro, CA	198
	Helm, CA	150
Arizona Agrochemical Co., subsid.	Chandler, AZ	40
Vulcan Materials Company Chemicals Division	Wichita, KS	35
The Williams Companies		
Agrico Chemicals Company, subsid.	Blytheville, AR	380
	Catoosa, OK	425
	Donaldsonville, LA	400
TOTAL		18,687

(a) From Stanford Res. Inst. Directory of Chemical Producers, 1976.

(b) Thousands of tons/yr.

(c) New capacity, addition 83, 1976.

(d) Addition 93, 1976.

(e) Addition 420, mid 1977.

(f) Addition 495, early 1978.

(g) Addition 412, 1976.

In the dehydration, the conversion of carbamate to urea is about 50 to 75%. The remainder is decomposed to ammonia and carbon dioxide. Variations among processes are directed primarily to economic disposal of this gaseous mixture.

Ammonia and carbon dioxide, in a mole ratio of about 3:1, are compressed to liquids and charged into a steam-heated, silver-lined reactor. The reactants require about 2 hr to pass through the reactor at 190°C and 1500 to 3000 psi. During this time the ammonia and carbon dioxide react to form ammonium carbamate which is largely converted to urea.

The reaction mixture, consisting of about 35% urea, 8% ammonium carbamate, 10.5% water, and 46.5% unreacted ammonia, is discharged from the autoclave and cooled to approximately 150°C. The melt is passed to an ammonia still, operating at 60°C, where 60 to 65% of the unconverted ammonia and any unreacted carbon dioxide are distilled and collected in an ammonia-absorption system. The yield of urea in the crude melt is 80 to 85%, based on the carbon dioxide.

The residue in the ammonia still, (consisting largely of urea and water), is crystallized at 15°C. About 70% of the remaining free ammonia is removed by vacuum and sent to the recovery system. The resulting slurry is centrifuged, separating the crystalline urea in about 50% yield. The mother liquor containing about 21% ammonium carbamate, 38% urea, 14% ammonia, and 27% water, is sent to the ammonia-recovery system, where it is used to make liquid fertilizer.

Urea was formerly made from calcium cyanamide, but development of high-pressure equipment allowed establishment of the ammonia-carbon dioxide process. The process is not standard and many modifications of the basic process exist.

Plants vary in capacity from 18,000 to 470,000 tons/yr. All plants are allied with an ammonia plant and can produce urea-ammonium nitrate or liquid fertilizer solutions.

Due to less expensive natural gas in other parts of the world, major new urea plants are being constructed outside the United States, so that by 1980 North America will be importing approximately one-third of its urea requirements.

Urea is used in making urea-formaldehyde resins which, because of their fire-retardant properties, are particularly useful as binders and adhesives for plywood, particle board and paper, wet-strength resins for paper, resins for coatings and molding compounds, and textile processing. Uses of urea are listed in Table 48; manufacturers are listed in Table 49 and shown geographically in Figure 22.

TABLE 48. Uses of Urea

Fertilizers	60%
Animal feeds	25%
Resins	10%
Other	<u>5%</u>
	100%

TABLE 49. Manufacturers and Plant Sites for Urea Production^(a)

Company	Location	Capacity ^(b)
Agway, Inc.	Olean, NY	75
Air Products and Chemicals Inc.	Pensacola, FL	23
Allied Chemicals Corp. Specialty Chemicals Division	South Point, OH	70
Union Texas Petroleum Division Agricultural Department	Geismar, LA Omaha, NB	245 140
American Cyanamid Company Agricultural Division	New Orleans, LA	145
Baker Industrial Corp.	Carlsbad, NM	n.a.
Borden Inc. Borden Chemicals Division Petrochemicals	Geismar, LA	220
CF Industrial, Inc	Tyner, TN	40
Donaldsonville Nitrogen Complex	Donaldsonville, LA	340
Fremont Nitrogen Complex	Fremont, NB	40
North Carolina Nitrogen Complex	Tunis, NC	170
Coastal States Gas Corporation Colorado Interstate Corp., Subsid Wycon Chemicals Company, Subsid.	Cheyenne, WY	50
Columbia Nitrogen Corporation	Augusta, GA	38
Cooperative Farm Chemicals Association	Lawrence, KS	269
Enserch Corporation Nipak, Inc., Subsid.	Kerens, TX Pryor, OK	70 102 ^(c)
Esmark, Inc. Swift Agricultural Chemicals Corp.	Beaumont, TX	51
Gardiner Big River, Inc.	Helena, AR	67
Gen. American Oil of Texas Premier Petrochemicals Company, Subsid.	Pasadena, TX	94
Goodpasture, Inc. Western Ammonia Corp., Subsid.	Dimmitt, TX	23
W. R. Grace and Company Agricultural Chemicals Group	Memphis, TN	138 ^(d)

TABLE 49. (Cont'd)

Company	Location	Capacity ^(b)
Hercules Inc. Synthetics Department	Hercules, CA Louisiana, MO	40 95
Kaiser Aluminum & Chemicals Corp. Kaiser Agricultural Chemicals Div.	Savannah, GA	129
Good Hope Indust. Inc.	Corpus Christi, TX	600 ^(e)
Mississippi Chemicals Corp.	Yazoo City, ms	140
N-Ren Corporation Cherokee Nitrogen Division	Pryor, OK	18
High Plains Division	Plainview, TX	45
Olin Corporation Agricultural Chemicals Div.	Lake Charles, LA	165
Phillips Pacific Chemicals Company	Kennewick, WA	38
Phillips Petroleum Company Fertilizer Division	Beatrice, NB	50
Reichhold Chemicals Inc.	St. Helens, OR	68
St. Paul Ammonia Products, Inc.	East Dubuque, IL	85
J. R. Simplot Company Minerals and Chemicals Division	Pocatello, ID	15
Skelly Oil Company Hawkeye Chemicals Co., Subsid.	Clinton, IA	61
The Standard Oil Company (Ohio) Vistron Corporation, Subsid. Chemicals Department	Lima, OH	220
Tennessee Valley Authority	Muscle Shoals, AL	61
Terra Chemicals Internat'l, Inc.	Port Neal, IA	160
Triad Chemicals	Donaldsonville, LA	470
Tyler Corporation Atlas Powder Company, Subsid.	Joplin, MO	74
Union Oil Co. of California Collier Carbon and Chemicals Corp., Subsid.	Brea, CA Kenai, AK	120 350

TABLE 49. (Cont'd)

Company	Location	Capacity ^(b)
United States Steel Corporation		
USS Agri-Chemicals Division	Cherokee, AL	25
Valley Nitrogen Producers, Inc.	El Centro, CA	149
	Helm, CA	24
The Williams Companies		
Agrico Chemicals Co., Subsid.	Blytheville, AR	330
	Catoosa, OK	210
	Donaldsonville, LA	200
TOTAL		5752

(a) From Stanford Res. Inst. Directory of Chemical Producers, 1976.

(b) Thousands of tons/yr.

(c) New Capacity, addition 82, mid 1976.

(d) 138 to 350, early 1976.

(e) 1976.

FIGURE 22. Geographical Distribution of Ammonia, Urea, and Acrylonitrile Production

ACRYLONITRILE

Acrylonitrile is produced by reacting a mixture of propylene (propene), ammonia, and air in the presence of a catalyst.

Propylene (90+%), ammonia, and oxygen are mixed and fed to a fluidized bed catalytic reactor. The catalyst is a supported molybdenum-based catalyst, such as 50 to 60% bismuth phosphomolybdate on silica. At 400 to 450°C, 0.5 to 2 atm pressure, and with a 10 to 20 sec contact time, the propylene is converted to acrylonitrile. The yield is greater than 70% of that theoretically obtainable: 1 lb of propylene yields 0.84 lb of acrylonitrile.

The reactor effluent goes to an absorption column, where it is water scrubbed to separate gases for recycle. The aqueous acrylonitrile from the bottom of the scrubber goes to a separator, where wet acrylonitrile is distilled. Acetonitrile from the product separator is also purified by distillation.

Acrylonitrile plastics show considerably promise for expansion. These low-cost, all-around plastics are tough, moldable, and resistant to heat, light, and solvents. Acrylic fibers (all acrylonitrile polymers or copolymers) have already captured more than 20% of the total synthetic fiber market with further growth expected. Uses of acrylonitriles are listed in Table 50.

TABLE 50. Uses of Acrylonitrile

Acrylic and modacrylic fibers	55%
ABS and SAN plastics	20%
Nitrile rubber	5%
Other	<u>20%</u>
	100%

Essentially all the acrylonitrile produced comes from plants using propylene as a raw material. All future manufacturing facilities will probably be based on propylene because of lower costs. Present manufacturing facilities are listed in Table 51 and shown geographically in Figure 22.

TABLE 51. Manufacturers and Plant Sites
for Acrylonitrile Production

<u>Company</u>	<u>Location</u>	<u>Capacity</u> ^(b)
American Cyanamid Company	New Orleans, LA	100
E. I. DuPont deNemours and Co., Inc.	Beaumont, TX	170
	Memphis, TN	130
Monsanto Polymers and Petrochemical Company	Chocolate Bayou, TX	230
Vistron Corporation (SOHIO)	Lima, OH	<u>190</u>
TOTAL		820

(a) Thousands of short tons/yr.

PHOSGENE (CARBONYL CHLORIDE)

Phosgene is manufactured by reacting chlorine with an equal amount, or slight excess, of CO in the presence of activated carbon. Dry CO and chlorine are passed through water-cooled iron tubes (5 cm diameter) filled with activated charcoal. The reaction to form phosgene is highly exothermic, so that heat removal is the limiting factor in reactor design. Reaction conditions are 200°C and 2 to 4 psig. In most cases the phosgene is used as it is made, so condensation of the product is not necessary.

Although it is technically feasible to make isocyanates by the direct reaction with CO (for example, toluene diisocyanate from dinitrotoluene), thus obviating the requirement for phosgene, it is not done at present. The reaction requires pressures of about 250 atm and a temperature of 150 to 190°C. Until a suitable catalyst is found whereby reaction conditions can be much reduced, phosgene will continue to be an important chemical intermediate in the manufacture of toluene diisocyanate, and hence of urethane plastics.

Uses of phosgene are listed in Table 52. The phosgene growth rate from 1963 to 1973 was 15% annually. It is estimated that it will grow through 1978 at 12%/yr. This rapid growth in production of phosgene since 1955 is due

TABLE 52. Uses of Phosgene

Toluene diisocyanate	62%
Other isocyanates	23%
Polycarbonates	6%
Other	<u>9%</u>
	100%

almost entirely to its use in the manufacture of isocyanates for polyurethane resins. Approximately 85% of phosgene produced is used in isocyanate manufacture. Future growth will depend on the demand for polyurethanes followed by polycarbonates and pesticides.

Polycarbonate resins are made from phosgene and bisphenol A. Their production increased from 1966 to 1969 at a compounded annual growth rate of 16%.

Because nearly all phosgene is used at the point of manufacture, most plants are captive. Two producers sell phosgene; however, they represent only about 5% of total capacity. Manufacturers and capacities of production are listed in Table 53, and shown geographically in Figure 23.

TABLE 53. Manufacturers and Plant Sites for Phosgene Production^(a)

Company	Location	Capacity ^(b)
Allied Chemical Corporation	Moundsville, WV	49
BASF Wyandotte Corporation	Geismar, LA	22
Chemetron Corporation	LaPorte, TX	40
E.I. duPont deNemours and Co., Inc.	Deepwater, NJ	68
FMC Corporation	Baltimore, MD	3
General Electric Company	Mt. Vernon, IN	30
Texaco Inc.		
Jefferson Chemical Company	Port Neches, TX	15
Mobay Chemical Company	New Martinsville, WV	120
	Baytown, TX	65
Olin Corporation	Ashtabula, OH	
	Lake Charles, LA	85
Ott Chemical Company (Story Chemical Corporation)	Muskegon, MI	5

Table 53 (continued 2)

Company	Location	Capacity ^(b)
PPG Industries, Inc.	Barberton, OH	2
Rubicon Chemicals, Inc.	Geismar, LA	62
Stauffer Chemical Company	Cold Creek, AL	12
Union Carbide Corp.	South Charleston, WV	55
Upjohn Company	LaPorte, Tx	150
Van de Mark Chemical Co., Inc.	Lockport, NY	4
TOTAL		787

(a) Thousands of tons/yr.

(b) SRI Directory of Chemical Producers, 1976.

FIGURE 23. Geographical Distribution of Phosgene and Diisocyanate Production

DIISOCYANATES

Diisocyanates, of which 2,4-toluene diisocyanate is representative, are made by reacting the corresponding diamine (or the amine hydrochloride) with phosgene, and separating the evolved hydrogen chloride. The reaction is usually carried out in the presence of a high-boiling solvent, from which the final product is separated by vacuum distillation. Monoisocyanates and other polyisocyanates are made by similar processes.

Toluenediamine (either the 2,4- or 2,6-isomer or a mixture of the two) is dissolved in an aromatic hydrocarbon or a halogenated derivative. The solvent mixture is then mixed with phosgene (1.5 to 3.5 lb phosgene/lb of diamine) in a reactor held at 20 to 50°C.

Another way to accomplish this initial reaction is contacting a solution of diamine with a solution of phosgene (both in the same solvent) at a somewhat lower temperature.

In either case the resulting slurry is pumped to a second reactor, where further reaction with gaseous phosgene occurs at 185°C. Unreacted phosgene and some liberated hydrogen chloride leave the top of the reactor.

The final conversion to diisocyanate occurs in a third vessel, where an inert gas is blown through the solution at 110 to 115°C. The resulting solution of crude 2,4-toluene diisocyanate is vacuum distilled.

The diisocyanates are predominantly used in the manufacture of urethanes (see Table 54). Urethane products are formed by reacting polyfunctional molecules containing active hydrogen, for example, polyether resins, with polyfunctional isocyanates. The product may be a foam, fiber, elastomer, coating, or adhesive. The largest single application for the urethanes is flexible polyurethane foam.

Rigid polyurethane foams are used primarily as insulating materials in buildings, household appliances, industrial refrigerators, refrigerated

TABLE 54. Use of Diisocyanates

Flexible polyurethane foams	54%
Rigid polyurethane foams	27%
Other	<u>19%</u>
	100%

truck bodies, and railroad cars. Production of both rigid and flexible polyurethane foams grew at an average rate of 21 and 15% respectively, from 1965 to 1970. Methylene Diphenyl Isocyanate (MDI) and 80/20 toluene diisocyanate (TDI) are the major isocyanates used in polyurethane applications.

Manufacturers of diisocyanates and their geographic locations are shown in Table 55 and Figure 23, respectively.

TABLE 55. Manufacturers and Plant Sites for Diisocyanate Production^(a)

Company	Location	Capacity ^(b)	
		TDI ^(c)	MDI ^(d)
Allied Chemical Corporation	Moundsville, WV	40	
BASF Wyandotte Corporation	Geismar, LA	45	
E.I. duPont de Nemours and Co., Inc.	Deepwater Point, NJ	52	
Texaco, Inc.			
Jefferson Chemical Company	Port Neches, TX		18
Mobay Chemical Company	Cedar Bayou, TX		
	New Martinsville, WV	120	45
Olin Corporation	Lake Charles, LA		
	Ashtabula, OH	65	
Rubicon Chemicals, Inc.	Geismar, LA	15	42
Union Carbide Corporation	South Charleston, WV	27	
Upjohn Company	LaPorte, TX		150
Dow	Freeport, TX	<u>50</u>	
		414	255

(a) Stanford Research Institute, Directory of Chemical Producers, 1976.

(b) Thousands of tons/yr.

(c) Toluene-2,4- and 2,6-Diisocyanates.

(d) Methylene Diphenylisocyanate.

POTENTIAL VALUE OF CARBON MONOXIDE IN ORGANIC CHEMICAL MANUFACTURE

The conversion of CO to organic chemicals is not a new subject; in fact, reviews dated 1940^(389, 390) show that it was considered promising nearly 40 years ago. Any chemicals now produced from petroleum sources (e.g., from ethylene) can be produced from carbon or from CO. Currently chemicals made from methane (natural gas) are almost invariably made via CO as an intermediate. In these cases it obviously makes sense to eliminate the energy wasteful methane steam-reforming step.

It would be possible in this section to list all organic chemicals currently made from petroleum which could easily be made from CO, and state that at some future time it might be necessary for economic reasons to make them from CO. However, considering the basic purpose of this study, to do so would be pointless.

Applying criteria to limit the scope of consideration of chemical uses for CO, it is obvious that:

1. Any use of CO as a replacement starting material for manufacturing a specific product must be capable of producing that product at least as cheaply from CO as from the currently used starting material.
2. Questions of availability, yield, market size, gas purity, and the amount of new technology and equipment needed for the replacement of an existing process by a parallel process based on CO must be considered in relation to the overall process chemistry before a use for CO is recommended for further consideration.
3. No new process is going to replace an existing one, with or without the threat of another oil embargo, unless it is economically justified on its own account.

Three examples will serve to illustrate the basic reasoning behind these criteria.

It has been suggested by Tamers⁽³⁹¹⁾ that benzene derived via lithium carbide and acetylene would be a good substitute for petroleum-derived benzene in gasoline. Based only on the chemistry, outlined below, there is no problem with this. (Calcium carbide has been substituted for lithium carbide, since this is currently made in large quantities and is cheaper.)

Based on known reactions, it can certainly be made to work. Should we then convert all benzene production away from petroleum sources and in favor of total synthesis, as Tamers suggests? Consideration of the yields and prices of the products is informative: Acetylene derived from calcium carbide would sell for about \$0.21/lb, based on the current market price of \$0.085/lb for calcium carbide. If a 100% yield of benzene is assumed, this would also cost \$0.21/lb to make from acetylene. Currently, benzene from petroleum sources sells for \$0.118/lb. This calculation was done assuming no costs for chemical conversion equipment, and no losses. Obviously, to make benzene economically from carbon using the above route, benzene from petroleum would have to cost at least \$0.25/lb.

The above example illustrates the trap of assuming that a good practical synthesis is also an economical one, but it did not directly involve CO (CO also is a by-product of calcium carbide manufacture). A similar example involving the use of CO is: (392, 393)

Here, CO and acetylene are reacted with one another in the presence of a palladium chloride catalyst, producing maleic (and fumaric) acid, which is heated to form maleic anhydride. Maleic anhydride is a major plastics intermediate, currently made by partial oxidation of benzene.

In the above synthesis two molecules of CO react with one molecule of acetylene, and a small amount of oxygen, to yield maleic anhydride. If the CO is assumed to be essentially free as a waste gas, the cost of the maleic anhydride is based solely on the cost of the acetylene which, as mentioned above, would be about \$0.21/lb from calcium carbide. Since 98 lb of maleic anhydride can theoretically be made from 26 lb of acetylene, the maleic anhydride would cost $\$0.21 \times 26/98$, or \$0.06/lb. Again, this allows no costs for chemical equipment and assumes a 100% yield, but since the present selling price of maleic anhydride made from benzene is \$0.37/lb, there is a considerable leeway. Also, calcium carbide is used to make the acetylene; CO is a waste product from calcium carbide manufacture. Putting the two together gives maleic anhydride. Thus, there is no transportation difficulty--both chemicals are available at the same site.

The above example shows a way of making a major industrial organic chemical--maleic anhydride--essentially from air, limestone, and coke, potentially up to six times cheaper than its current price with savings in the use of petroleum-derived benzene which is now used for the production of maleic anhydride. Thus, this example may be a viable use for waste CO, whereas the direct synthesis of benzene was not.

Although the synthesis of maleic anhydride from air, limestone, and coke is essentially a hypothetical exercise at present, the example illustrated in Figure 24 shows that these materials are more widely used than is often realized. The figure shows how, with one modification to existing technology and current practice, and two revivals of obsolete processes, polyurethanes may be made from just these basic materials.

The examples also show another useful indicator: Generally, it will be uneconomical to make a reduced substance (e.g., benzene) from a more oxidized one, in this case, CO. To make an oxidized substance (e.g., acetic acid or

FIGURE 24. Formation of a Polyurethane Resin from Readily Available Materials (Carbon, Limestone, Air, and Water) Without Using Petroleum

maleic anhydride) from CO will probably be more economical. This guideline is based on a number of factors, including free energy change, increase in product molecular weight relative to starting materials, etc. Conversion of CO to methane (SNG) or gasoline is an exception, but there are special factors operating here.

Thus the following discussion will deal with only likely and actual candidates for chemicals production from waste CO, based on the reasoning already outlined above. No attempt will be made to include all materials which can potentially be made from CO.

HYDROGEN

Although hydrogen is not listed as a bulk chemical derived from CO, like CO, it is produced on a large scale but is used directly by the producer. Hydrogen is made for manufacturing methanol and ammonia, as well as a host of other materials. The methods used to make hydrogen include partial oxidation of light hydrocarbons;^(394,395) split stream steam reforming and oxidation of natural gas.^(396,397) Direct steam-reforming of methane (in natural gas),^(398,399) or liquid hydrocarbons is more common.⁽⁴⁰⁰⁻⁴⁰²⁾ The reaction of methane with carbon dioxide has also been proposed,⁽⁴⁰³⁾ but is not used. The usual method chosen by industry is direct steam-reforming

of natural gas (methane) to a mixture of CO and hydrogen (Equation 1) followed by the water gas-shift reaction to convert the CO to hydrogen (Equation 2) if pure hydrogen is desired.

Equation 1 is the reverse of the CO methanation reaction, currently being hailed as the most effective way of making synthetic natural gas (SNG) from hydrogen and CO produced by the gasification of coal.

The CO shift reaction (Equation 2, above) has been used in making hydrogen for almost a century and has been steadily improved throughout the years (e.g., 404-413). Current developments in the field of shift conversion are concentrated mainly in the areas of new catalysts,^(9,29,30,414-421) automatic process control,⁽⁴²²⁾ and studies on the kinetics and mechanism of the shift reaction.^(423,424)

There has been considerable interest in recent years in the generation of hydrogen through thermochemical cycles. It is not generally realized that hydrogen production from CO is part of a thermochemical cycle, when the CO is generated from organic material and the energy input into the cycle comes from sunlight. The use of transition metal halides has been suggested.^(31,425) One example of such a cycle is:⁽⁴²⁵⁾

The net effect is the conversion of water into its elements.

The natural "thermochemical cycle" which is carried out is as follows:

In both cases, CO_2 is recycled, and in both cases hydrogen is split off from water. In the natural-based cycle, the energy input is in the form of low-grade energy (sunlight), while in the artificial cycle, high temperatures are required (about 1000°K). Also, in the carbon cycle many fewer units of mass are transported to generate a unit of hydrogen, since no heavy elements are involved.

The concept of the thermochemical cycle for hydrogen production is not new. Thermochemical processes have been proposed using the waste heat from phosphoric acid production, employing oxidation of some of the phosphorus with steam or carbon dioxide.^(426,427) In the latter case, the CO generated was shifted to hydrogen. Since phosphorus is normally oxidized anyway, (by air) to make food-grade phosphoric acid, oxidation with steam did not alter the products and also produced by-product hydrogen. The reaction of metals with steam has been used as a way of making hydrogen,⁽⁴²⁸⁾ as for example in the familiar iron/steam reaction:

With a reductant such as CO, this is another way of shifting CO to hydrogen:

There is a great variety of methods for making hydrogen. Some more exotic ones that have been proposed involve a tin oxide/tin/steam reaction using CO as the reductant,⁽⁴²⁹⁾ and the steam/air reforming of methanol to hydrogen and CO.^(430,431)

The trends in hydrogen production methods identified in this brief survey indicate that:

- hydrogen production via the water gas shift reaction from CO will remain the chief synthetic route to hydrogen,
- natural gas and petroleum are used to make CO via steam-reforming; this will gradually be supplanted by CO made by the gasification of coal or organic residues
- thermochemical cycles based on elements other than carbon offer little promise as future economical sources of hydrogen from water-splitting.

HYDROCARBONS

Methane and other hydrocarbons are formed from CO and hydrogen in a series of conversions collectively known as the Fischer-Tropsch reaction.

Methane

Methanation is the conversion of CO or CO₂ to methane.⁽⁴³²⁻⁴³⁴⁾ In the case of CO, the process is:

The basic conversion written above actually involves several competing reactions:

Thus, the methanation of CO (1) is concurrent with the conversion of CO to hydrogen (2), the methanation of CO₂ (3), and the decomposition of CO to carbon and carbon dioxide (4). At the normal methanation temperature of about 870°C, the two methanation reactions are very exothermic. The consequences

of this are twofold; 1) the methanation process rate is limited by the capacity of the equipment to remove waste heat,^(435,436) and 2), the overall energy efficiency of the conversion is lowered because the heat evolved during methanation is lost. It is a simple matter to calculate the energy efficiency of methanation of CO by hydrogen (E):

$$E = \frac{\text{Total heat evolved by burning CO} + 3\text{H}_2}{\text{Total heat evolved by burning CH}_4} = \frac{67.5 + 3(68.3)}{211}.$$

This relation holds because from Equation (1), one mole of methane is formed from one mole of CO and three moles of hydrogen. The value for E is 0.775, indicating that in the conversion of CO to methane, the theoretical energy efficiency is 77.5%, assuming zero process losses. In simple terms, this means that if all of the nation's natural gas were made by methanation of coal-derived CO with hydrogen, at least 22% of the energy in this coal would be lost.

The subject of the mechanism of methanation has been dealt with in a thorough fashion by Seglin et al.,⁽⁴³⁷⁾ in a book devoted to the subject of methanation of synthesis gas, and by Dalla Betta et al.⁽⁴³⁸⁾

Attempts to increase the efficiency of the methanation process have been somewhat successful, and involve novel reactor configurations to remove process heat,⁽⁴³⁹⁻⁴⁴²⁾ liquid phase methanation,^(443,444) more efficient catalysts,^(438,445) and combining the water gas shift reaction with the methanation step,⁽⁴⁴⁶⁻⁴⁴⁸⁾ using the water to moderate the reaction:

However, the process is more complex than appears from the conversions written above, since the carbon dioxide will itself react exothermically with hydrogen:

There is also the possibility of the reverse reaction, steam reforming of methane, regenerating CO and hydrogen. The overall effect is complex. Methanation of carbon dioxide has received some interest,⁽⁴⁴⁹⁻⁴⁵¹⁾ but this process offers little advantage over CO methanation since it uses more hydrogen and generates more water.

Conversion of hydrocarbon oils to methane via partial oxidation followed by methanation has been suggested.⁽⁴³⁴⁾ Although this would be one way of converting a surplus petroleum fraction into gas, it is inherently a very wasteful process.

Methanation is being seriously considered because existing pipelines carry methane (natural gas), which is in increasing short supply. Carbon monoxide cannot be substituted directly for methane because it has a lower heating value per unit volume (67.5 kcal/mole compared with 211 kcal/mole for methane). Higher pipeline pressures, adjustments to equipment, and a number of other difficulties would occur if CO were substituted for methane in gas pipelines.

Thus, methanation may be a way to convert coal to synthesis gas and then to synthetic natural gas (SNG), on a large scale. This may be economical because of the existence of a distribution system already operating with natural gas. However, the methanation of industrial waste CO, makes little sense. Industries which use fuel gas and produce CO (e.g., iron and steel), already have equipment to burn CO directly as a fuel and thus alleviate the need for the more expensive natural gas. To convert their CO to SNG would entail replacement of existing equipment and acceptance of a 22% energy loss. To use the CO made by one industry, convert it to SNG by methanation, and then add it to the natural gas pipeline distribution system would also not be desirable. In this case, the quantities of CO available at any one location would likely be too small to justify the expense of the equipment. It is very likely that in the future, SNG will be made from coal-derived producer gas on a massive scale, and that any unit doing the same from industrial waste CO would be too small to be competitive.

Other Hydrocarbons

It is possible to generate hydrocarbons other than methane from the reaction of CO with hydrogen. This is the traditional meaning of the term "Fischer-Tropsch Reaction," although the broad term includes any materials which can be made directly by reacting CO with H₂. The exact composition of the product is a function of reaction conditions and catalyst composition. For instance, it is possible to make 100% methane using a platinum based catalyst, while the alternative iron, nickel, or ruthenium based catalysts generate large proportions of C₄ and higher hydrocarbons.⁽⁴⁵²⁻⁴⁵⁷⁾

The Fischer-Tropsch reaction generated considerable interest when it was first discovered, since it offered a means of synthesizing complex organic chemicals from simple gaseous feedstocks. Although this is still true, the availability of cheap natural gas and the cost of the equipment required to perform the reaction (which occurs at high temperature and pressure) have tended to minimize the impact of the discovery, to the extent that at present only one country in the world (S. Africa) uses Fischer-Tropsch syntheses commercially on a large scale. The Sasol plant there is used to produce gasoline. Despite a recent accident in the plant⁽⁶¹⁾ there are plans to build a second plant of three times the capacity. However, this decision, like the original one, was politically rather than economically motivated.

Synthetic gasoline has long been the aim of innovators, particularly since the realization that petroleum supplies are limited. Methanation and pyrolysis have been suggested as ways of boosting the yield of higher hydrocarbons from the Fischer-Tropsch reaction,^(458,459) but by far the most promising recent development has been new specific zeolite catalysts⁽⁴⁶⁰⁻⁴⁶²⁾ which are "tunable" to a variety of product distributions, from ethylene to aromatics. Theoretical and mechanistic studies,^(457,463) and research results on metal carbonyl homogeneous catalysts^(464,465) promise further developments in the near future. The wider application of Fischer-Tropsch

reactions in chemical syntheses from CO-containing feedstocks will depend both on new technology and on improved economics over present conditions.

ALCOHOLS

Hydrocarbons are not the only products of the Fischer-Tropsch synthesis. With the correct conditions and catalysts, alcohols may be made from CO and hydrogen. The primary alcohol produced by this method in industry is methanol (the production of which has already been described). Higher alcohols may also be made by this route, but in practice they are made using another reaction involving CO, hydrogen, and an unsaturated hydrocarbon (the Reppe and Oxo syntheses).

The purpose of this section is to bring together related alcohol synthesis reactions so that they may be seen in the proper perspective, and to indicate trends in development of improved processes which may have future importance.

Methanol

The production of methanol in industry involves a form of the Fischer-Tropsch reaction. Although it is technically possible to make methanol by the partial oxidation of methane,⁽⁴⁶⁶⁾ the simultaneous formation of formaldehyde and formates constitute yield and separation problems. The equation for methanol formation by the Fischer-Tropsch reaction is:

Methanol may be made from carbon dioxide by reduction with hydrogen, but this uses up an additional molecule of hydrogen just to make water and is thus less favored, although small amounts of carbon dioxide are no great problem in the normal synthesis from CO and hydrogen:⁽⁴⁶⁷⁾

Originally there was considerable difficulty in making methanol, since hydrocarbons were formed almost entirely, or the catalysts were poisoned. This problem was finally solved after discovering that the steel vessels

used were catalyzing hydrocarbon formation (iron is a good catalyst for this), and the resulting iron and nickel carbonyls formed were poisoning the methanol synthesis catalyst.^(468,469) Values of 60 mg/l of iron in the methanol product were recorded.⁽⁴⁷⁰⁾ Erosion of the steel pressure vessel also constituted a hazard. By improving the equipment and catalysts it was possible to avoid iron carbonyl formation to a large extent,⁽⁴⁷¹⁾ although even today it is necessary to refine the product methanol to remove carbonyl^(472,473) and other impurities.^(474,475) Variations on the overall process were tried, such as using excess hydrogen,⁽⁴⁷⁶⁾ or dilution of the synthesis gas with inert gas,⁽⁴⁷⁷⁾ but a stoichiometric ratio of $\text{CO}:\text{H}_2$ is now invariably used. Many other process improvements have been reported for methanol (and ammonia) reactor configurations and process techniques,⁽⁴⁷⁸⁻⁴⁹⁵⁾ including a large-scale plant design to produce 8000 tons/day,⁽⁴⁹⁶⁾ and a description of the use of mathematical modeling and computer control in optimizing process parameters in large production plants.^(497,498)

The trend today is to integrate the methanol synthesis loop with a synthesis gas production unit (some form of air or oxygen-blown gasifier, or hydrocarbon oil or natural gas steam-reformer),⁽⁴⁹⁹⁻⁵⁰²⁾ and advances are being made in the simultaneous liquid phase shift reaction between CO and water coupled with methanol synthesis from CO and the hydrogen formed,⁽⁵⁰³⁾ and in the liquid phase synthesis of methanol from synthesis gas.⁽⁵⁰⁴⁾ Homogeneous catalysts (e.g., iron carbonyl) have now been found to be effective in the liquid phase, for making methanol.^(505,506) It is apparent from the recent literature that methanol synthesis technology is not stagnant.

Catalyst development has kept pace with the improvements in apparatus and the depth of knowledge of the methanol synthesis reaction.⁽⁵⁰⁷⁾ Almost all of the many catalysts reported have been of the spinel or zeolite structure, impregnated with various metal oxides and promoters.^(404,503,504,508-577) Copper, zinc, and chromium or boron figure largely in the composition of the more successful catalysts. All have the disadvantage of being easily poisoned by hydrogen sulfide and other sulfur compounds. Recent work on nonpoisonable sulfide-based methanol synthesis catalysts has shown some indication of success, although the idea was first patented in 1934.⁽⁵⁵⁸⁾

Although catalyst development has been a gradual evolution rather than a discontinuous series of major improvements, catalysts are now so effective that methanol is made at much lower pressures and temperatures than originally. Recently, for example, a patent was issued⁽⁵⁵⁹⁾ for methanol synthesis using a copper/vanadium/zinc/manganese oxide-based catalyst, using a pressure of 300-1200 psig and 200-300°C instead of the original 3000 psig at 350°C. Other catalysts have been reported with similar efficiencies.⁽⁵⁶⁰⁻⁵⁶³⁾ Most of this work was done before there was any clear understanding of the mechanism of catalyst action during methanol synthesis, and in fact the mechanism is still far from well known. Recent examples of work done on this important subject include studies of gas composition effects,^(564,565) adsorption on catalyst surfaces,⁽⁵⁶⁶⁾ solid solution effects,⁽⁵⁶⁷⁾ and a tracer study showing a clear difference in reaction mechanism for methanol synthesis when iron or when oxide catalysts are used.⁽⁵⁶⁸⁾

Further significant improvements in the efficiency of methanol synthesis may be expected, due to the high level of current research and the large scale of methanol production.

Higher Alcohols

Although methanol is always a major product of the Fischer-Tropsch class of reactions where oxide catalysts are employed, higher alcohols are also formed, probably by carbonylation of the intermediate methanol coupled with reduction with hydrogen. In practice these alcohols are made by the Oxo synthesis, where CO reacts with hydrogen in the presence of an alkene (olefin). A third type of reaction involves alcohol synthesis from CO, hydrogen, and an alkyne (acetylene), and is known as the Reppe reaction, after its discoverer. All three types of higher alcohol synthesis may involve metal carbonyl catalysis, and have been reviewed by Falbe.⁽⁵⁶⁹⁾ Although separate reactions, there is often confusion between the three types. Here, the following definitions apply:

Hydrogenation products of these are included in the definitions, as are minor products caused by further reactions of the initial major products. Advances are being made in the state-of-the-art of these reactions, which have always suffered from the general problem of yielding a wide range of products unless highly specific catalysts are employed. Current production of organic chemicals is limited to the Oxo synthesis, in which ethylene, CO and hydrogen are combined to make propanols and butanols, and other olefins used to make 2-ethylhexanol and decanols (e.g., 570-575). Use of the Fischer-Tropsch reaction for higher alcohol synthesis was claimed generally in a 1931 patent,⁽⁵⁷⁶⁾ and has since been improved.^(577,578) Use of alcohols as starting materials with CO and hydrogen has also been recommended.^(579,580) Alcohols up to octadecanol have been isolated from these reactions.⁽⁵⁸¹⁾ Further recent developments include the use of molten iron catalysts,⁽⁵⁸²⁾ and a study of the mechanism of iron catalysis of this reaction.⁽⁵⁸³⁾ The combination of the water gas shift reaction with the Fischer-Tropsch synthesis has also been shown to work.⁽⁵⁸⁴⁾ A novel specialized synthesis of trialkylmethanols (trialkylcarbinols) has been demonstrated, using an organoborane to transfer an alkyl group to CO.⁽⁵⁸⁵⁾ This involved reaction of CO with a hydrogen source (aluminum hydride), and although technically not a Fischer-Tropsch reaction, may be applicable to the synthesis of specialized higher alcohols that are otherwise difficult to make.

The most significant advance in CO/H₂ conversion is the synthesis of glycols directly from synthesis gas. The high pressure synthesis of ethylene and propylene glycol was described⁽⁵⁸⁶⁻⁵⁹⁰⁾ in a series of patents granted in 1976 to Union Carbide Corp., wherein CO was reacted with hydrogen at up to 50,000 psig and 150-300°C in the presence of an organic solvent and a homogeneous catalyst consisting of rhodium carbonyl and a trialkanolamine borate. Improvements in catalyst activity and reduction of the severity of the reaction conditions are anticipated. If the reaction can be made economical, a major petroleum chemical (ethylene glycol) may in the future be made from synthesis gas.

Since butylene glycol has been carbonylated to adipic acid⁽⁵⁹¹⁾ (another petroleum chemical of major importance), an increase in the scope of the

glycol synthesis to a four-carbon unit would further erode the importance of petroleum in chemical synthesis. An alternative synthesis of the butylene glycol would be by hydrogenation of butyne-1,4-diol, which has been made by the Reppe synthesis from formaldehyde and acetylene.⁽⁵⁹²⁾ Both formaldehyde and acetylene are accessible from carbon, hydrogen, and CO.

ALDEHYDES, KETONES, AND ESTERS

Apart from a few major industrial chemicals such as methanol and acetic acid, and intermediate bulk organic chemicals such as acrylates, butanol and propanol, CO is little used for making organic chemicals. Many materials have been made from CO by carbonylation reactions in the laboratory, and which have the potential for industrial applications.

The Fischer-Tropsch, Reppe, and Oxo syntheses all have the disadvantage of generating mixtures of products which are usually difficult to separate into their individual components. For instance, depending on the catalyst and conditions, methanol and CO will react to form a variety of acids, esters, aldehydes and higher alcohols.⁽⁵⁸⁰⁾ Despite this, CO does have product specificity in a number of related reactions.⁽⁵⁹³⁾ These will be reviewed briefly in the following sections.

Aldehydes

Formaldehyde

Although formaldehyde can theoretically be made from CO and H₂ by the reaction:

in practice none is made by this route. Instead, all of the formaldehyde generated in the U.S. is made by the partial oxidation of methanol. The reasons for this are: 1) formaldehyde is usually used in a location remote from a source of producer gas, 2) methanol is a liquid which is easy to transport, and 3) formaldehyde made from producer gas is mixed with other aldehydes, and is difficult to purify.

Formaldehyde is made by the reaction:

A second reaction occurs also, based on direct dehydrogenation:

Other Aldehydes

Other aldehydes are made primarily by the Oxo reaction, in which both alcohols and aldehydes are formed. However, the carbonylation reaction is not specific for the terminal position of the alkyl group and generates both primary and secondary alcohols and the corresponding aldehydes. For a number of years this was a major problem in the Oxo synthesis of butanol from propylene, CO, and hydrogen:^(594,595)

Catalyst developments have now essentially solved the problem for butanol and butanal synthesis, but it still exists with other aldehydes [e.g., or from 1-dodecene⁽⁵⁹⁶⁾]. Special applications have been found to give good yields of particular aldehydes, as for instance in the preparation of 3,7-dimethyl-1-octanal,⁽⁵⁹⁷⁾ where a 72.5% selectivity for the No. 1 position of the starting alkene occurred.

The possibility of making alkaloids directly from CO and an alkene was raised by the discovery of a complex cyclotricarboxylation/reduction reaction in which a relatively simple alkene (3,3-dimethylcyclopropene) was converted to a mixture of homotropane derivatives⁽⁵⁹⁸⁾ (Figure 25). There is a need for more research to determine whether this type of synthesis can be used to make other plant-derived alkaloid precursors for pharmaceutical use.

Although generally nonspecific, carbonylation reactions can be made stereospecific by the use of an optically active reactant, as in the case of α -phenylpropanal synthesis from synthesis gas and styrene in the presence of optically active methylphenylbenzylphosphine and a rhodium complex catalyst.⁽⁵⁹⁹⁾ This suggests that carbonylation reactions may be made highly specific with sufficient attention to detail.

FIGURE 25. Homotropane Derivatives from Carbon Monoxide and Alkenes⁽⁵⁹⁸⁾

Ketones

Normally ketones may not be made by any of the three major reaction modes previously described (Fischer-Tropsch, Reppe, Oxo reactions). However, it is possible to alter the stoichiometry of the carbonylation reaction such that two molecules of an alkene combine with one molecule of CO to form ketones:

The catalyst required is dicobalt octacarbonyl.^(600,601) Recently, the reaction has been significantly improved by using an alkylcopper complex,⁽⁶⁰²⁾ and extended to give high yields (78-100%) of diaryl ketones from the cobalt

carbonyl-catalyzed carbonylation of diarylmercury compounds.⁽⁶⁰³⁾ Cyclic ketones such as cyclopentanone have been prepared by decomposition of a titanium complex prepared using ethylene and CO,⁽³²²⁾ and benzofuranones have been prepared by the high pressure reaction of CO with cresols.⁽⁶⁰⁶⁾

Esters

Acrylates

Methyl and ethyl acrylate are currently made on an industrial scale by the Reppe reaction between acetylene, CO, and hydrogen in the presence of nickel carbonyl catalyst. Some acrylic acid is made in a similar fashion using CO. Propylene oxidation is also used to make acrylic acid, but this route does not involve CO. The use of a dilute acetylene stream to carry out this reaction has been proposed and shown to be effective,⁽⁶⁰⁵⁾ thus minimizing the explosion hazard from concentrated acetylene streams.

Other Esters

Olefin carbonylation may be used to make almost any ester, provided that suitable starting materials are used. The process has been patented in a general sense.⁽⁶⁰⁶⁾ A number of modifications have been proposed to the general process, such as the use of ketone,⁽⁶⁰⁷⁾ water or ether⁽⁶⁰⁸⁾ reaction promoters, organic solvents such as benzil,⁽⁶⁰⁹⁾ new catalysts⁽⁶¹⁰⁻⁶¹²⁾ and methods of catalyst recovery.⁽⁶¹³⁾ The conversion of methanol to methyl acetate has been patented.⁽⁶¹⁴⁾ This reaction involves the carbonylation of methanol, and would normally yield acetic acid or methyl formate.⁽⁶¹⁵⁾ However, by selection of suitable catalysts and conditions a 60% yield of methyl acetate was obtained, with only 10% of acetic acid being formed. Acetaldehyde dimethyl acetal is another product of this reaction when cobalt carbonyl catalysts are used.^(616,617) Many other esters have been synthesized by carbonylation, including methylene dipropionate⁽⁶¹⁸⁾ (with the addition of propionic acid and formaldehyde to the reaction mixture), nonadienoate esters⁽⁶¹⁹⁾ trimethylolpropane carboxylates,⁽⁶²⁰⁾ dialkyl malonates (from ethyl chloroacetate),⁽⁶²¹⁾ propyl butyrate and amyl caproate from propyl and amyl ethers,⁽⁶²²⁾ long chain ethylenic acid esters,^(623,624) alkyl aryl acetates,^(625,626) methyl formylvalerates,⁽⁶²⁷⁾ lactones from diolefins or diols,⁽⁶²⁸⁾ and β -alkoxypropionic acid esters.⁽⁶²⁹⁾ This list is not

all-inclusive, but gives some indication of the versatility of carbonylation reactions in organic synthesis. Many of the above-mentioned compounds have some specific industrial use, and are currently made by more complex synthetic routes or isolated from natural products.

An interesting synthesis of alkyl esters under mild conditions has been reported,⁽⁶³⁰⁾ in which a stream of CO is bubbled at -70°C into a liquid acid medium containing sulfur dioxide, hydrogen chloride, antimony(V) chloride, and a tertiary alcohol or substituted olefin, giving up to 97% yields of tertiary carboxylate esters. Mild conditions of this nature should promote industrial interest in this reaction, despite the acid nature of the solvent and catalyst systems.

ACIDS, AND ACID DERIVATIVES

Acids

Formic Acid and Sodium Formate

Traditionally, sodium formate has been made by passage of CO under pressure (50 atm) at 210-240°C into 40% aqueous sodium hydroxide solution.⁽⁶⁷³⁾ No sodium formate is made in the U.S. by this route today; instead formate salts and formic acid are made as by-products of butane oxidation.

The alkali/formate production can be represented by the equation:

The production of formic acid and sodium formate by this route from waste industrial CO is uneconomical, since the demand is low (31,000 tons/yr), and there is excess capacity for formate production as a by-product from butane oxidation (to acetaldehyde).

There is some potential for use of the alkali absorption of CO as a way of purifying gas streams and trapping the CO, but even this use appears to have been co-opted by the appearance of the COSORB process.

Bethlehem Steel Corp. is reported⁽⁶³¹⁾ to have developed a process for CO reaction in aqueous alcohol solutions, which generates formate esters. Hydrolysis of the ester yields formic acid directly, and a recyclable alcohol. However, even this process, which avoids the production of sodium salts, may be of little economic value. The process may be represented as:

There have been three recent reports of improvements in the synthesis of sodium formate from CO and sodium hydroxide.⁽⁶³²⁻⁶³⁴⁾ No new processes have been developed.

Acetic Acid

Acetic acid production is still largely achieved by partial oxidation of butane, but this process is now being supplanted by the newer route involving carbonylation of methanol. This is a case where a major industrial chemical may now be made more cheaply and efficiently than previously, as a direct result of research in high pressure carbonylation chemistry. Patents owned by the Monsanto Co. are being licensed to Daicel Ltd.⁽⁶³⁵⁾ for the production of 200,000 tons/yr of acetic acid from methanol, and a part of the synthesis gas which will be produced by du Pont and National Distillers will be similarly used to make acetic acid.⁽⁶³⁶⁾ Although methanol carbonylation has been known for a number of years, conditions were too severe for the reaction to be industrially economical or acceptable. Improvements in catalysts⁽⁶³⁷⁻⁶⁴²⁾ are now being reported. In view of the potential profitability of the Monsanto process, it probably will not be long before even more efficient catalysts are discovered.

Higher Monocarboxylic Acids

Theoretically, carbonylation of an alcohol is a general reaction which may be used to increase chain length and convert an alcohol into an acid:

However, synthesis of higher acids by carbonylation has not been performed by this route. Instead, ethylene may be hydrocarboxylated to propionic acid,⁽⁶⁴³⁾ or alkyl formates, acetates and benzoates carbonylated in the presence of a mercury catalyst.⁽⁶⁴⁴⁾

A very efficient way of making tertiary carboxylic acids has received considerable attention recently. This involves the addition of CO to the tertiary alkyl carbonium ion generated by reaction of a geminally di-alkyl substituted alkene (olefin) with a powerful Lewis acid. Yields approaching 100%

have been achieved by passing CO at atmospheric pressure and at -70°C into solutions of the Lewis acid and the olefin. Some of the Lewis acids which have been found effective are sulfuric acid, (with a cuprous salt or carbonyl catalyst), boron trifluoride, antimony pentachloride in liquid sulfur dioxide, and anhydrous hydrogen fluoride.^(630, 645-656) Compounds which can eliminate small molecules to form olefins, such as tertiary halides and alcohols, will also react,⁽⁶⁵⁷⁾ but the synthesis is currently limited to tertiary acids because the use of primary or secondary starting materials leads to skeletal rearrangements and isomer formation. Copper carbonyl in sulfuric acid at $20-50^{\circ}\text{C}$ will also catalyze the carbonylation reaction of olefins to tertiary acids.⁽⁶⁵⁸⁾

A synthesis with potential industrial value which has recently been reported involves the conversion of acetylene by the Reppe reaction to maleic anhydride, maleic acid, and fumaric acid.^(392, 393) A palladium catalyst was used, in the presence of oxygen. Although very simple in principle (as shown below), practical synthesis of maleic anhydride from acetylene and CO requires further work. This should be worth while, as maleic anhydride is a chemical of major industrial importance.

Dicarboxylic Acids

Oxalic acid is the simplest member of this series; it is derived from organic wastes, from heating sodium formate, or as a by-product from citric acid manufacture. Currently, Pfizer makes it by the latter route. Oxalic acid is a potential derivative of formic acid and hence of CO, but the low value (\$0.22/lb), poor market stability and volume (16,000 tons/yr), and ready accessibility of alternative sources other than CO make it a poor candidate product from waste CO.

There is no reason in principle why diols could not be carbonylated on both alcohol groups to produce dicarboxylic acids, since the reaction with a single

alcohol group (e.g., methanol to acetic acid) is known to work. This reaction has now been shown to be practicable in the synthesis of adipic acid from butanediol.⁽⁵⁹¹⁾

Adipic acid is a major component of nylon.

Potassium malonate has been prepared by carbonylating potassium carbonate and acetate.⁽⁶⁵⁹⁾ Unsaturated acids may also be carbonylated to produce dicarboxylic acids,⁽⁶⁶⁰⁾ but usually a mixture of isomers is obtained. Unsaturated dicarboxylic acids have been prepared by the Reppe reaction with acetylenes and CO, using an excess of CO in an organic solvent.⁽⁶⁶¹⁾

Substituted Acids

Carbonylation syntheses are not restricted to saturated and unsaturated acids. Glycolic acid (hydroxyacetic acid) and oxydiacetic acid have been prepared by carbonylation of formaldehyde,⁽⁶⁶²⁾ and methyl glycolate has been made from carbonylation of methylene sulfate.⁽⁶⁶³⁾ Glycolic acid acetate is made from formaldehyde, CO, and acetic acid.⁽⁶⁶⁴⁾

Perhaps the most significant recent report on advances in carbonylation reactions to generate acids is the claim that good quality citric acid has been made by a carbonylation of an unspecified intermediate.^(665, 666) By analogy with other reactions, the most likely intermediate for this novel and important synthesis would be dihydroxyacetone:

Anhydrides

Acetic, propionic, heptanoic and benzoic anhydrides have been prepared by the carbonylation of the corresponding ester (methyl acetate, propionate, ethylhexyl heptanoate, and phenyl benzoate, respectively).⁽⁶⁶⁷⁻⁶⁷⁰⁾ Methyl iodide, iodine, or a metal iodide was used as a catalyst.

The synthesis of maleic anhydride by the Reppe reaction between acetylene, CO, and oxygen in hydrogen chloride has already been mentioned. It may be

possible to extend this reaction to other cyclic dicarboxylic anhydrides. 2-Methylsuccinic and glutaric anhydrides have been prepared by a different route, involving the dicarbonylation of allyl alcohol.⁽⁶⁷¹⁾

Acid Chlorides

Not only acids and anhydrides, but acid chlorides may be made directly by carbonylation. Reaction of 1,2,3-trichloropropane with CO and hydrogen chloride yielded dichloroisobutyryl chloride by CO insertion in a C-Cl bond.⁽⁶⁷²⁾ Presumably this reaction may be extended to the preparation of other acid halides.

Amides

Amides have been prepared by direct carbonylation of olefins in the presence of ammonia or amines.⁽⁶⁷³⁻⁶⁷⁵⁾

AMINES, AMIDES, ISOCYANATES, AND RELATED COMPOUNDS

Carbon monoxide has been used as a major reactant in the synthesis of a wide variety of nitrogen-containing compounds, both by direct carbonylation and through the more reactive derivative, phosgene (carbonyl chloride). These reactions are difficult to classify, since for the most part they were directed towards specific chemicals of interest rather than general classes, or involved a series of intermediates which were all isolable. For example, an aromatic nitro compound may be reduced by CO through the nitroso, hydroxamate, and amino functions; each of these intermediates can be made to react through carbonylation as well as reduction (excepting the nitro group), yielding imines, nitriles, amides, heterocycles, and isocyanates. An alkene may undergo a form of the Reppe reaction in which ammonia is present, or an amine, or other of the above reactive intermediates, and form amines and amides with increased functionality. Thus, rather than attempting an exhaustive review and classifying all of these reactions according to type, it is more useful and less confusing to give examples of the major reactions and to reference their more obscure applications.

Amines, Imines, Nitriles

Ammonia

Ammonia is not formed directly from CO, but is made using the hydrogen produced from CO by the water gas shift reaction.⁽⁶⁷⁶⁻⁶⁸¹⁾ In fact, since an iron catalyst⁽⁶⁸²⁾ or iron-group catalyst⁽⁶⁸³⁾ is used in ammonia synthesis by the Haber process, the presence of CO leads to carbonyl formation and thus to problems of catalyst poisoning, reactor erosion, and product contamination. The ammonia synthesis gas must be pre-purified to eliminate CO.⁽⁶⁸⁴⁾

Amines

N-Alkylamines may be prepared by reacting CO, hydrogen, and ammonia in the presence of a catalyst,⁽⁶⁸⁵⁾ in a process analogous to the Fischer-Tropsch reaction. Reaction of dimethylamine with CO and water over an iron/copper/potassium carbonate catalyst has been shown to lead to formation of long chain (C₁₋₂₆) alkyl dimethylamines.⁽⁶⁸⁶⁾ It seems likely that this occurs by carbonylation of the dimethylamine to an amide, followed by reduction. Tertiary amines have also been prepared by the reaction between CO, a secondary amine, a ketone, and water.⁽⁶⁸⁷⁾

Aniline can be prepared from nitrobenzene by the copper-chromium oxide catalyzed reduction reaction with hydrogen in the presence of CO.⁽⁶⁸⁸⁾ This is more economical than the metal/acid reduction of nitrobenzene and in fact a similar reduction process using hydrogen as the reductant is superseding the iron/acid reduction process. In a related CO reduction reaction, azoxybenzene was prepared from nitroso-benzene.⁽⁶⁸⁹⁾

Imines

Imines, azomethines, or Schiff bases are intermediates in the reduction of nitro compounds to amines. An imine can be made in 60-84% yield by the combination of an aldehyde with a nitro-compound in the presence of CO and rhodium carbonyl catalyst.⁽⁶⁹⁰⁾ The amine and isocyanate analogs were excluded as intermediates, and the role of CO identified as one of direct reduction. Schiff bases, once formed, may undergo carbonylation to produce phthalimidines or indazolones,⁽⁶⁹¹⁾ of potential value in pharmaceutical syntheses.

Nitriles

These are not normal products of carbonylation reactions, although a recent patent assigned to du Pont describes the formation of nitriles from aromatic halides by reaction with metal cyanates and CO in the presence of nickel or palladium catalysts.⁽⁶⁹²⁾

Amides

Alkylamides and Arylamides

Alkylamides may be made by the direct reaction between ammonia or amines. Ammonia reacts with CO to form formamide.⁽⁶⁹³⁾ N,N-Dimethylformamide is made similarly, using dimethylamine instead of ammonia.⁽⁶⁹⁴⁾ Higher alkylamides are made somewhat differently, from hydrogen cyanide, CO and a higher alcohol.⁽⁶⁹⁵⁾ Formamides derived from isobutylamine, diethylamine, and piperidine have been made by carbonylation of the amine in the presence of a mercury acetate catalyst,^(696, 697) but some amines form dialkyl- or diarylureas (e.g., aniline forms diphenylurea). However, aniline may be converted to formanilide (= phenylformamide) with CO in the presence of hydrogen selenide.⁽⁶⁹⁸⁾ Similarly, 2-aminopyridine may be carbonylated to formamidopyridine (= 2-pyridylformamide),⁽⁶⁹⁹⁾ and some amino alcohols have been found to form N-(hydroxyalkyl) formamides with CO and mercuric acetate.⁽⁷⁰⁰⁾

A new synthesis of calcium cyanamide has been reported, using ammonia, CO, and limestone.⁽⁷⁰¹⁾ Calcium cyanamide is normally made by heating calcium carbide and nitrogen. Technically, calcium cyanamide is the calcium salt of cyanoamine ($\text{NH}_2\text{-CN}$), isomeric with diimine (NH=C=NH), and is not an amide. It is included here because the name "calcium cyanamide" is used universally.

Urea and Derivatives

Urea is a special case of an amide, and is made on a large scale from carbon dioxide and ammonia, by isomerization of ammonium carbamate.⁽⁷⁰²⁾ Although the present synthesis method seems very satisfactory, urea can be made by a facile reaction between CO and ammonia at 11-31 atm pressure and temperatures of 132°C or greater.^(703, 704) The urea is withdrawn as a liquid.

Substituted ureas can be made by a similar process, using an amine instead of ammonia, and reacting it with CO. The reaction appears to require some form of sulfur. For instance, tetramethylurea was prepared from dimethylamine, CO, and elemental sulfur.⁽⁷⁰⁵⁾ Carbanilide (diphenylurea) was made using

carbonyl sulfide, CO, water, and nitrobenzene.⁽⁷⁰⁶⁾ Diphenylurea has also been prepared using a palladium/alumina catalyst and in the presence of ferric chloride,⁽⁷⁰⁷⁾ or a tertiary phosphine or amine.⁽⁷⁰⁸⁾ Recently, selenium/triethylamine catalysts have been found effective in this reaction,^(709, 710) and nitro- or nitroso-compounds have been shown to react similarly.⁽⁷¹¹⁾ Selenium catalysts appear to have general activity in the area of CO reactions with amine and nitro-compounds, since they also catalyze the formation of carbamates (RNHCOOH) from amines, alcohols, and CO,⁽⁷¹²⁾ and selenium was found to react with CO and ethylenimine at 20°C and atmospheric pressure to form a polyseleno-carbamate (ethylenimine/CO/selenium copolymer).⁽⁷¹³⁾

Isocyanates

The isocyanate group, -N=C=O, is one of great importance in polymer chemistry, since isocyanates will polymerize with glycols to form polyurethanes. Polyurethanes are a class of plastics of considerable value in modern usage. To form polymers, two isocyanate groups are required to be attached to the same molecule. The simplest such compound is carbonyl diisocyanate [CO(NCO)₂].⁽⁷¹⁴⁾

Current technology for making isocyanates involves the reaction of an acid chloride (phosgene) with an amine.⁽⁷¹⁵⁾ This is the same method that has been used for many years in making acyl chlorides,⁽⁷¹⁶⁾ and which involves the generation and use of phosgene on a large scale. Union Carbide's proposed synthesis gas plant at Institute, WV, will generate CO to be used in part for methyl isocyanate production,^(717, 718) presumably via phosgene. Phosgenation is technically well understood, but involves the generation of a very toxic gas (phosgene) and the use of chlorine as a chemical activating agent. This chlorine has to be regenerated. The cycle is represented by the equations:

If isocyanates could be made directly, much chemical manipulation and expense would be saved. The aim of current research in this area is to effect the direct conversion:

Alternately the reducing action of CO can be employed to start directly with aromatic nitro-compounds which are the precursors for aromatic amines:

The direct insertion of CO into a C-Cl bond has been shown in the formation of carbamoyl chloride from chloramine and CO.⁽⁷¹⁹⁾ To perform the equivalent reaction with an amine, a palladium catalyst was needed.⁽⁷²⁰⁾ Isocyanates were formed. Similar carbonylation reactions occurred with aromatic nitroso, and azo-compounds and azides,⁽⁷²¹⁾ using palladium carbonyl chloride polymer as the reactant, but substituted ureas and other intermediates were formed as well as isocyanates. Aromatic isocyanates were produced directly from the equivalent nitro-compounds at 37% conversion efficiency, using a nickel and molybdenum-based catalyst at high temperature (190°C) and very high pressure (562 atm of CO).⁽⁷²²⁾ There is considerable Japanese activity in this area,^(723, 729) as well as European.⁽⁷³⁰⁻⁷³³⁾ Most of the European work as well as the U.S. work, is assigned to the Olin Mathieson Corp.⁽⁷³⁴⁾

Currently, direct isocyanate synthesis is directed at making toluene-2,4-diisocyanate directly from 2,4-dinitrotoluene. This is one of the primary urethane intermediates made today. Work is needed in the areas of catalyst development and improving reaction yields and decreasing the formation of by-products. Temperature conditions are acceptable (ca. 190°C), but very high CO pressures are still needed to effect the conversion. The pressure requirement will have to be reduced drastically before direct carbonylation will be economically more advantageous than the low-pressure synthesis using phosgene.

Heterocyclic Compounds

The versatility of carbonylation as a route to chemical intermediates is illustrated by the wide variety of heterocyclic compounds which can be made. Heterocyclic compounds are chiefly used in pharmaceutical synthesis, and in

pesticides. Since the specific heterocyclic compound to be made will vary with the end use of the product, there is more value in general methods for carbonylation rather than in isolated special cases. Carbonylation is in fact a general reaction, as was shown in a recent article describing the preparation of classes of heterocyclics with 5, 6, and 7-membered rings from CO and compounds of general formula $H_2N(CH_2)_3XH$, where "X" is oxygen or sulfur.⁽⁷³⁵⁾ Selenium was used as a catalyst in these reactions. Cyclo-carbonylation has been used in the preparation of 2-pyrrolidone,⁽⁷³⁶⁾ cyclic thiocarbonates,⁽⁷³⁷⁾ benzazoles, benzazolinones, quinolines and indoles,⁽⁷³⁸⁾ indazolones,⁽⁷³⁹⁾ 2,4,5-trialkylimidazoles and N-acyl- α -aminoketones,⁽⁷⁴⁰⁾ and urazoles.⁽⁷⁴¹⁾ Most of these reactions used easily accessible intermediates.

CARBON MONOXIDE-DERIVED POLYMERS

Carbon monoxide has considerable utility in polymer chemistry, as has already been seen in its use for making isocyanates. Such a use may be considered indirect, since the polymer is made from an intermediate, where the intermediate was produced using CO or phosgene. Another indirect application of CO in polymer chemistry is its use as an initiator in ethylene homopolymerization.⁽⁷⁴²⁻⁷⁴⁴⁾ However, CO is involved directly as a monomer in a number of new polymers which are currently generating considerable interest. These are copolymers of CO and an unsaturated hydrocarbon, such as ethylene,⁽⁷⁴⁵⁾ and may be prepared using a palladium-based catalyst.⁽⁷⁴⁶⁾ They have some interesting properties, such as being photodegradable in sunlight,^(747, 748) and UV light,⁽⁷⁴⁹⁾ having photoconductivity,⁽⁷⁵⁰⁾ and conferring improved heat molding characteristics on polyvinyl chloride.⁽⁷⁵¹⁾ Acetylene/CO/water plasma polymers have been produced which are effective reverse osmosis membranes,⁽⁷⁵²⁾ giving 94% salt rejection at a water flux of 32 gal/ft²/day. Such membranes offer promise for the separation of pure water from sea water without distillation. Finally, the use of CO/ethylene polymer oxime copper chelates has already been mentioned as a promising new method for separation of CO from dilute gas streams.⁽³³⁴⁻³³⁶⁾

The use of CO in polymers appears to have been missed for many years, which is odd as the unsaturated nature of the $C\equiv O$ bond appears ready-made for polymerization reactions. However, polymers made using CO and the related compound, CO₂,⁽⁷⁵³⁾ are now being studied and offer considerable promise for future application in industry.

OTHER POTENTIAL USES FOR CARBON MONOXIDE

As a Reducing Agent

Mixtures of CO with hydrogen or water have been used as selective hydrogenating agents in organic synthesis,⁽⁷⁵⁴⁻⁷⁵⁷⁾ where they act without causing isomerization.

Inorganic uses for CO as a reducing agent include the recovery of non-ferrous metals from oxide ores and concentrates,⁽⁷⁵⁸⁾ and iron recovery from oxides⁽¹⁰⁰⁻⁷⁵⁹⁾ and sulfates.⁽⁷⁶⁰⁾ Direct reduction with CO is a useful method for making metals on a small scale.

The reduction of sodium sulfate⁽⁷⁶¹⁾ and gypsum (calcium sulfate)^(195, 372) directly to the sulfides by CO has been proposed. The sulfides are of use in the paper industry. Where sulfates are recovered at all, they are already effectively reduced to sulfides by the incomplete combustion of pulp liquors. A more innovative application of CO in the paper industry is its use for selectively reducing lignin in the presence of a metal carbonyl catalyst, producing a liquid oil and pure cellulose.⁽⁷⁶²⁾ The cellulose is suitable for paper making.

For Chemical Production

Carbon monoxide has been proposed as an intermediate in the manufacture of carbonyl sulfide,^(763, 764) and hydrogen sulfide⁽⁷⁶⁵⁾ by direct synthesis. However, both of these are normally accessible as by-products and are unlikely to be made as primary products. The chlorination of cerium oxide with CO and chlorine has been suggested.⁽⁷⁶⁶⁾ Exotic inorganic chemical reagents (e.g., chloroformyl fluorosulfonate⁽⁷⁶⁷⁾) and organometallic carbonyls⁽⁷⁶⁸⁾ may also be made using CO.

Fuel Desulfurization

Treating mercaptans with CO at 80-300°C and 30-150 atm pressure will convert them to hydrocarbons and carbonyl sulfide.⁽⁷⁶⁹⁾ This reaction could be of value in the "sweetening" of petroleum, and has been patented for this purpose.⁽⁷²⁰⁾ Coals and chars can also be desulfurized by CO.⁽⁷⁷¹⁾

Liquid Fuel Production

Treatment of coal or cellulosic materials with water and CO under pressure results in formation of a liquid product, which after stabilizing and refining may be suitable as a liquid synthetic fuel.^(772, 773)

Other Uses

Carbon monoxide has been investigated and found to be effective as a component of rocket fuels,⁽⁷⁷⁴⁾ as an accelerant in the nitriding of ferroalloys,⁽⁷⁷⁵⁾ and as a substrate for bacterial cell growth.⁽⁷⁷⁶⁾

CONCLUSIONS

The list of uses for CO ranges from the very large scale (methanol, ammonia, phosgene, etc.) to the very small, such as some of the specialty chemicals listed previously. Its potential as a chemical feedstock appears likely to grow considerably in the future, with the advent of CO-based light degradable polymers, plasma membranes, and urethane intermediate synthesis by direct carbon-ylation. The preceding section was not written with the intent of being exhaustive, but instead to indicate the potential value of CO as a chemical feedstock rather than as a fuel or a waste gas.

COMPARISON OF CARBON MONOXIDE AND METHANE AS FUEL OR CHEMICAL FEEDSTOCK

At first glance carbon monoxide appears to be inferior to methane as a fuel. Carbon monoxide is a toxic, odorless gas with a gross heating value only about a third of that of methane (322 vs. 1013 Btu/ft³, respectively (see Table 56).

However, methane contains hydrogen which forms water upon combustion. Although the heat of condensation (vaporization) of this water is usually lost, it is allowed for in natural gas marketing. Natural gas is generally priced on the basis of its gross heating value, which includes the heat of condensation of the resulting water vapor. Assuming that natural gas is pure methane (actually, natural gas compositions can vary considerably according to source of supply), then the gross heating value exceeds the net heating value by 10%. Although the heat of condensation of the water vapor might be recovered in some very special instances, the dewpoint of the flue gas stream is usually too low to allow its recovery.

Another consideration in comparing carbon monoxide and methane as fuels is the fact that every volume of methane burned produces three volumes of combustion products (carbon dioxide and steam) while CO burns entirely to produce an equal volume of carbon dioxide:

Table 56 indicates that combustion of carbon monoxide yields 8944 ft³ of flue gas (60°F, 30 in. Hg) per 10⁶ Btu generated (theoretical). Combustion of methane, however, yields 11,533 ft³ of flue gas per 10⁶ Btu generated; a 29% increase in flue gas volume for equivalent heat obtained.

Apart from the disadvantage of the additional volume of flue gas to be handled, the flue gas is often exhausted at elevated temperatures and thus contains sensible heat. Assuming a flue gas exhaust temperature of 500°F, about 8.5% of the heating value of carbon monoxide is lost as sensible heat in the flue gas. When methane is burned, this loss increases to about 18.8% (assuming the same exhaust temperature) because of the unrecoverable heat of condensation

of the water vapor formed. Thus, about 10 percent more fuel value is lost when burning methane than when burning carbon monoxide. Therefore, although carbon monoxide is inferior to methane on a heating value per unit volume of fuel basis, burning methane results in a higher percentage of heating value lost in the flue gases. Additional considerations of mass and energy utilization of these two gases are discussed below.

TABLE 56. Comparative Data on Carbon Monoxide and Methane (Natural Gas)

		Heat Value			Cubic Feet			Pounds	
		Gross	Net(a)	Net	ft ³ Air	ft ³ Flue	ft ³ Flue	Gas per	Hydrogen
		Per	Per	Btu/	Required	Gas/ft ³	Gas per	10 ⁶ Btu	Producible
		ft ³	ft ³	lb	Per ft ³	Gas	10 ⁶ Btu	(net)	Per 10 ⁶
					Combustion	Burned	(net)		Btu (Net)
Carbon Monoxide	CO	322	322	4347	2.38	2.88	8944	230	16.30 ^(b)
Methane (natural gas)	CH ₄	1013	913	21520	9.53	10.53	11533	46.5	17.7 ^(c)

(a) Btu/ft³, 60°F and 30 in. Hg, dry.

(b) Via reaction: $\text{CO} + \text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{CO}_2$ (slightly exothermic).

(c) Via reaction: $\text{CH}_4 + 2\text{H}_2\text{O} \longrightarrow 4\text{H}_2 + \text{CO}_2$ (highly endothermic). This figure also allows for CH₄ which is usually burned to supply the heat for the steam reforming reaction as practiced on an industrial scale.

SOURCE: Chemical Engineers' Handbook, 5th Edition. R. H. Perry, Editor, McGraw Hill, New York, NY, 1973, p. 9-16.

The principal chemical use for methane is for hydrogen and CO production via the steam reforming reaction:

This reaction is highly endothermic.

Carbon monoxide can also be converted directly to hydrogen by the shift reaction:

This reaction is slightly exothermic.

Since hydrogen is used in the production of major chemicals (ammonia, methanol, urea, formaldehyde, and others), and since it can be derived either from methane or CO, it is a good basis for comparing the value of methane and CO as a chemical feedstock. Of course, some major chemicals are not made using hydrogen, (e.g., acetic acid from carbonylation of methanol) and thus would require different parameters for comparison of natural gas and CO.

The effectiveness of hydrogen production from either methane or CO is illustrated as follows:

From methane:

or 1 volume of methane yields 4 volumes of hydrogen with a large endothermic overall heat of reaction.

From carbon monoxide:

or 1 volume of CO yields 1 volume of hydrogen with a small exothermic heat of reaction.

Thus, on a volume (or mole) basis, CO does not appear to be favorable when compared with methane for hydrogen production (unless the CO is of much lower equivalent cost).

Both methane and CO may be regarded as gaseous fuels and, therefore, may likely be marketed on the basis of heat value such as dollars per million Btu's. Since CO yields no water on combustion, its net and gross heat values are identical. The two gases, therefore, should be compared on the basis of their net heat values: 322 Btu/ft³ for CO and 913 Btu/ft³ for methane.

On this basis, 322 Btu's (1 ft³) of carbon monoxide feedstock are required to produce one cubic foot of hydrogen. Production of hydrogen from methane, however, requires 228 Btu's ($\frac{913}{4}$) per cubic foot of hydrogen produced. Therefore, on a Btu basis, hydrogen synthesis from carbon monoxide requires 41 percent more feedstock than does hydrogen synthesis from methane. Thus, if methane (natural gas) is marketed at \$2.00/million Btu (net heat value basis) CO might be expected to command a market price of \$1.42 per million Btu (\$2.00/1.41). The above analysis does not account for any differences in capital and operating costs for the methane and carbon monoxide to hydrogen conversion facilities.

ECONOMICS OF BY-PRODUCT CARBON MONOXIDE COLLECTION, TRANSPORTATION, AND CONVERSION

The most advanced technology today for collecting CO from mixtures of gases is the COSORB process developed by Tenneco Chemicals, Inc. The copper liquor process used in the past has recently been supplanted by cryogenic separation methods. It has been claimed that COSORB is more economical than cryogenic separation and is thus the most economical method for obtaining CO from gas mixtures. Comparative carbon monoxide recovery process costs are shown in Table 57.

TABLE 57. Comparative Costs for Carbon Monoxide Recovery(263)

	<u>Plant Capacity</u>	<u>Capital Required</u>
COSORB	100 x 10 ⁶ lb/yr	\$2.25 x 10 ⁶
Cu Liquor	96	3.17
Cryogenic	87.3	3.35

In a study such as this, it is important to be able to place a value on the CO which can be derived from waste industrial off-gases both at the production site and at a distance, since this determines whether CO recovery is an economical proposition.

For any off-gas CO to be recovered, it may have to be (a) concentrated, and (b) purified. It may then have to be transported to its place of use. In the COSORB and cryogenic processes, the gases must be thoroughly dry. In the COSORB process, impurities such as hydrogen sulfide and sulfur dioxide must also be removed in a pre-purification step because they react irreversibly with the active component in the solvent, cuprous aluminum chloride.

The degree of purification of the concentrated CO will depend on its intended use, and the particular impurities to be removed from the off-gas will vary from industry to industry. In addition, the particular impurities present in the CO stream will also be a function of the source--elemental phosphorus from phosphorus industry byproduct CO, metal fluorides from aluminum, etc. It is, therefore, very difficult to place a general figure on the cost of CO purification. However, the cost of concentration may be calculated approximately. For this calculation, the most advanced process currently available (COSORB) has been chosen.

Estimated Capital and Operating Costs for COSORB Process

The basis chosen is a COSORB plant which processes 5000 scf/min of CO (99% pure) from a gas stream containing 15 vol% CO, 5 vol% carbon dioxide with the balance nitrogen and other inerts. The plant includes a gas dryer, COSORB absorber, COSORB stripper, heat exchangers, pumps, instrumentation, and COSORB solvent recovery from the absorber off-gas via refrigeration.

The calculated capital and operating costs for this COSORB plant are shown in Tables 58 and 59.

We have been advised of a similar study by Tenneco Chemicals Inc. personnel. This study is based on blast furnace gas at 20% CO, and about three times the production basis used above. The study estimated fuel production costs to be $\$0.48/10^3 \text{ SCF}$ (\$1.50/million Btu) of recovered CO, compared to our result of $\$0.98/10^3 \text{ SCF}$ (\$3.04/million Btu). No initial value for the CO was assumed in either case.

TABLE 58. Estimated Capital Cost
of COSORB Plant

Item	Cost ^(b)
COSORB Plant ^(a)	\$5,000,000
Refrigeration, 200 tons at 0°F	230,000
Solvent, Chemicals, Supplies and COSORB Licensee Fee	<u>350,000</u>
	\$5,582,000

(a) R. G. Minet, Kinetics Technology International Corporation, San Marino, CA, Private Communication, October 5, 1976.

(b) Mid-1976 basis.

TABLE 59. Estimated Operating Costs
of COSORB Plant

Labor, Maintenance, Overhead, etc.	
Direct Labor, one/shift at \$14,000/yr	\$ 56,000
Supervision, at 20% of D.L.	11,000
Labor Overhead, at 30%	20,000
Plant Maintenance, at 4% of Capital Cost	223,000
General and Administrative Costs, at 1.5% Capital Cost	84,000
Chemicals and Supplies	<u>50,000</u>
TOTAL	\$ 444,000
Utilities:	
Steam, 40,000 lb/hr at 150 psig, \$1.50/1000 lb	518,000
Electrical, 1242 kW at \$0.02/kWh	215,000
Cooling Water, 900 gpm at \$0.03/1000 gal	<u>14,000</u>
TOTAL	747,000
Capital Charges (Interest, Taxes, Depreciation, Insurance, etc.) at 20% of Capital Cost	<u>1,116,000</u>
TOTAL ANNUAL OPERATING COST	\$2,307,000
SCF Produced: $(7.2 \times 10^6 \text{ scf/d CO, 99\% pure, 330}$ operating days per year), 2,352.24 million SCF/yr	
$\frac{\text{Annual Operating Cost}}{\text{SCF/yr}} = \frac{\$2,307,000}{2,352.24 \times 10^6} = \$0.98/10^3 \text{ SCF}$	

Comparison of Cost of Transporting Hydrogen and Carbon Monoxide Through a Pipeline

In some situations CO may be more valuable as a chemical intermediate for the production of hydrogen, methanol, ammonia, urea, and derived chemicals than as a fuel. However, the quantities of waste or underused CO obtained from some chemical plants are so small that building a CO utilization plant to produce the aforesaid chemicals is uneconomical. In such a situation, it may be desirable to build a centralized CO utilization plant, which uses the waste CO from more than one CO byproduct source.

A key factor in operating such a plant economically is the cost of transporting gas from production sites to the plant through a pipeline system. Depending upon the chemical produced, the gas used in the plant can be either pure hydrogen, as in ammonia production, or a combination of CO and hydrogen as in methanol and urea production. If hydrogen is used in the plant, waste CO can be either directly transported to the plant and then converted to hydrogen, or CO can be converted to hydrogen at the source and the resulting gas transported by pipeline to the plant. The choice between these two alternatives will depend on the availability of small-scale CO shift converters and the cost of gas transportation.

The cost of transporting a gas through a pipeline is roughly a function of kind of gas to be transported, size of pipe to be used, pressure of gas and the cost of pipe, compressor, and labor. To operate a CO utilization plant economically the cost of gas transportation must be minimized. The cost study in the following section is aimed at identifying the most economical way of transporting gas.

To compare the cost of various modes of transporting gas through a pipeline the following assumptions were made:

- 10^6 Btu/min of gas were to be transported through a pipeline 100 miles long.
- Gas to be transported was either CO or hydrogen.

- The source pressures of CO and hydrogen were assumed to be 14.7 psia.
- Two different delivery pressures of gas, 14.7 psia and 500 psia were considered.
- The pipeline system was considered as a grass-roots facility.
- The cost for transporting gas through the pipeline system included: pipeline, compressor station, energy and labor cost.

The results of this comparison are summarized in Figures 26 and 27. Natural gas (Methane) costs are included for purposes of comparison.

FIGURE 26. Annual Cost of Gas Transportation (1×10^6 Btu/min). Case 1: Initial and final pressure 14.7 psi.

FIGURE 27. Annual Cost of Gas Transportation (1×10^6 Btu/min).
Case 2: Initial pressure 14.7 psi and final pressure 500 psi

The cost of the pipeline was found to be a major portion of the total transportation cost, especially when the diameter of the pipe was large. When the pipe diameter was small (8 in. and 6 in.), the cost of energy became a predominant factor. In Case I, where delivery pressure was 14.7 psia, the minimum cost of hydrogen transportation was found to be about $\$0.298/10^6$ Btu and the optimal pipe diameter about 9 in.; the cost of CO transportation was about $\$0.405/10^6$ Btu and the optimal pipe diameter 12 in. In Case II, where delivery gas pressure was 500 psia, the minimum cost of transporting hydrogen in the range of conditions studied was $\$0.426/10^6$ Btu and the optimal pipe diameter 6 in.; the minimum cost of transporting CO was about $\$0.483/10^6$ Btu and the optimal pipe diameter 7.5 in. In both high and low delivery pressure cases the cost of transporting hydrogen, on an equivalent Btu basis, is less than that for

CO. The difference in delivery cost between the two gases becomes less significant when gas is delivered at high pressure, because energy costs become a significant cost factor.

A sensitivity analysis indicated that changes in the cost of the pipeline and energy costs were most critical and that changes in the cost of the compressor station less critical to the total gas transportation cost. (See Appendix A.)

The cost of transporting hydrogen in all cases was less than the cost for transporting CO. Thus, if the quantity of available waste CO from a plant is not large enough to support construction of a CO utilization plant, and if operation of small scale CO shift conversion plants to produce hydrogen is economically feasible, it would be advantageous to convert CO to hydrogen and transport the resulting hydrogen to the point of utilization when hydrogen is the desired feedstock.

Additional details of this study, including calculations, are contained in Appendix A.

PRELIMINARY ECONOMIC EVALUATION OF PRODUCING AMMONIA AND METHANOL FROM CARBON MONOXIDE

The industrial off-gas streams cataloged in this study contain a wide range of CO concentrations and a variety of other constituents. Some of these gas streams will be better suited, economically, as feedstocks for certain chemicals than for others. Gas cleanup requirements for the removal of particulates and impurities which act as catalyst poisons will vary greatly from situation to situation. (See Appendix B for a discussion of catalyst poisons.) In many instances the carbon monoxide content of the off-gas stream is dilute and concentration of CO via COSORB or one of the other purification processes will be required prior to use as a chemical feedstock.

Local conditions at a specific industrial site, such as the availability of excess steam, will have a large impact on the economics of chemical production from waste carbon monoxide. Local and regional demand for a specific chemical commodity as well as transportation costs will also have a large influence on the selection and production cost of a specific chemical. Thus, each situation with potential for the production of chemicals from waste CO must be evaluated on its own merit.

During the course of this study it became apparent that a preliminary indication of the value of carbon monoxide as a chemical feedstock was desirable. Ammonia and methanol synthesis were chosen for this preliminary evaluation because they are both major chemical commodities and enjoy wide geographical consumption in the U.S.

Both ammonia and methanol can be prepared from a wide range of hydrocarbon feedstocks, including coal. In the United States natural gas is by far the dominant feedstock for both methanol and ammonia synthesis.⁽⁷⁷⁷⁻⁷⁸⁰⁾ As the price of natural gas has increased, emphasis has increased on higher plant efficiencies.⁽⁷⁸¹⁾ This factor, and others, has led to rapid escalation in the capital costs of ammonia and methanol plants.

Methanol and ammonia plants have definite economies of scale up to capacities of at least 1000 tons/day. Many sources of waste CO cannot provide synthesis gas for plants larger than 300-400 tons/day. For this preliminary economic evaluation we have chosen as a base case the off-gas from a typical elemental phosphorus plant with a capacity of about 140,000 tons/year. The off-gas was assumed to be 98% CO (890 tons/day) and 2% CO₂ available at atmospheric pressure and ambient temperature. Gas cleaning requirements were not included in the estimate. Preliminary flowsheets and material and energy balances were prepared for both plants. Capital equipment costs were estimated from published sources.^(777, 780-783) Prime movers (compressors and pumps) were assumed to be electrically driven. Neither flowsheet was optimized in terms of temperature and pressure to find the least cost combination.

Ammonia Production Economics

In a conventional ammonia plant utilizing steam reforming of natural gas the process sequence is:

- Primary Reformer. Natural gas is heated together with steam at pressure (200-800 psig) in the presence of a catalyst to produce CO and hydrogen via the reaction:

This reaction is highly endothermic and complete conversion does not take place at higher pressures. For this evaluation reformer heating was assumed to be provided by natural gas.

- Secondary Reformer. Conversion of the methane to CO and hydrogen is completed in this step. Air is combined with the partially reformed synthesis gas just prior to this step to provide sufficient nitrogen for the formation of ammonia later in the process. The oxygen from the air reacts with a portion of the methane and/or CO to form carbon dioxide.
- Shift Conversion. In this stage of the process, steam is combined with the gas from the secondary reformer over a shift catalyst to convert most of the carbon monoxide to hydrogen via the water gas shift reaction:

- Carbon Dioxide Removal. At this point the carbon dioxide formed in the reforming and shift conversion steps is removed; usually by scrubbing with hot carbonate or monoethanolamine solutions.
- Final Purification. At this stage the small amounts of residual carbon oxides, which would poison the ammonia synthesis catalyst, are removed. This is usually done by methanation per the following reactions:

- Final Compression and Synthesis. In this final stage ammonia is produced by the reaction of hydrogen and nitrogen at 2000 to 5000 psig over a catalyst.

The process sequence for the synthesis of ammonia from CO used in this evaluation was:

- Compression to 400 psig. For this evaluation CO was assumed to be available at atmospheric pressure. This cost is not normally incurred in a conventional plant since natural gas is usually available at pressure.

- Shift Conversion. Again, CO is converted hydrogen via the water gas shift reaction. The conversion was assumed to be carried out in three stages, with interstage cooling to limit temperature buildup. Due to the pure nature of the CO, a semi-lean stage of carbon dioxide removal was assumed after the first stage of shift conversion.
- Carbon Dioxide Removal. The capacity of this section will be relatively large for a plant producing ammonia from CO compared to an equivalent conventional ammonia plant because all of the hydrogen requirement is obtained via the water gas shift reaction. The heat requirement for regeneration of the carbon dioxide absorption solution can have a large effect on process economics. The Benefield "hot carbonate" process was used for carbon dioxide removal in this evaluation.
- Nitrogen Addition. For this evaluation nitrogen was assumed to be provided by a conventional air separation plant at 99.5 percent purity. Ammonia plant design engineers at Pullman-Kellogg suggested this approach would be more economical than using compressed air to provide the required nitrogen since the latter approach would consume too much CO in converting the oxygen present in the air to carbon dioxide.⁽⁷⁸¹⁾ Nitrogen costs are based on an Airco-owned plant supplying nitrogen on an "over the fence basis."⁽⁷⁸⁴⁾ Compression from 40 psia to approximately 370 psia is required for the nitrogen stream.

Estimated capital and operating costs for a conventional 1200 ton per day ammonia plant operating on natural gas are shown in Table 60. If the cost of natural gas is $\$2/10^6$ Btu, the production cost of ammonia is estimated to be $\$138.81/\text{ton}$.

Estimated costs for the production of ammonia from CO are tabulated in Table 61. With an equivalent fuel cost ($\$2/10^6$ Btu), the cost of producing ammonia from CO is estimated to be $\$149.71/\text{ton}$. The current market price for ammonia is about $\$175.00/\text{ton}$ delivered.

TABLE 60. Estimated Capital and Operating Costs for the Production of Ammonia from Natural Gas

Basis: Mid 1976 Gulf Coast estimates for a conventional 1200 ton per day plant consisting of primary reformer, secondary reformer, shift converter, acid gas removal, methanation, and ammonia synthesis loop operating 330 days per year.

I. Capital Cost

Capital, Plant	\$58,000,000
Working Capital, startup costs, etc.	<u>8,700,000</u>
Total Fixed Investment	\$66,700,000

II. Annual Operating Costs

Feedstock, natural gas, 24.6×10^6 Btu/ton @ \$2/10 ⁶ Btu	19,483,000
Catalysts and chemicals	495,000
Utilities:	
Fuel, 9.4×10^6 Btu/ton @ \$2/10 ⁶ Btu	7,445,000
Electrical Power @ \$.02/kWh	131,000
Makeup water @ \$.60/Mgal	250,000
Cooling Water Circulation @ \$.03/Mgal	560,000
Waste Treatment @ \$.75/Mgal	<u>53,000</u>
	8,439,000
Operating Labor, 36 @ \$22,000/yr (includes benefits)	792,000
Supervision, @ 20% of Operating Labor	158,000
Maintenance, @ 4% of Capital Plant	2,320,000
General Administrative and Overheads @ 100% of Labor and Supervision	950,000
Taxes and Insurance, @ 2% of Capital Plant	1,160,000
Depreciation, 10% S.L.	5,800,000
R.O.I., 25% before Taxes on Capital Plant plus 10% on Working Capital	<u>15,370,000</u>
Total Annual Operating Costs	\$54,967,000

III. Operating Costs per ton of ammonia 138.81

TABLE 61. Estimated Capital and Operating Costs for the
Production of Ammonia Synthesis Gas from
Carbon Monoxide

Basis: Mid-1976 Gulf Coast estimates for a 345 ton per day ammonia plant consisting of carbon monoxide compression, shift conversion, acid gas removal, methanation, steam generation, nitrogen compression and ammonia synthesis loop operating 330 days per year. Nitrogen purchased over the fence.

I. Capital Costs

Capital, Plant

Carbon monoxide compression and shift conversion	\$7,935,000	
Carbon dioxide removal and methanation	4,387,000	
Ammonia synthesis loop and compressor	8,146,000	
Steam generation and nitrogen compression	<u>3,143,000</u>	
Capital Plant Total		\$23,612,000
Working Capital, etc.		<u>4,000,000</u>
Total Fixed Investment		\$27,612,000

II. Annual Operating Costs

Feedstock, 890 Tons/day CO		--
Nitrogen, over the fence		600,000
Catalysts & Chemicals		170,000
Utilities:		
Fuel, @ \$2/10 ⁶ Btu	\$3,817,000	
Electrical Power, @ \$.02/kWH	335,000	
Makeup Water, @ \$.60/Mgal	342,000	
Cooling Water Circulation @ \$.03/Mgal	400,000	
Waste Treatment, @ \$.75/gal	<u>32,000</u>	
	4,926,000	
Operating Labor 24 @ \$22,000/yr (Includes benefits)	528,000	
Supervision, @ 20% of operating labor	106,000	
Maintenance, @ 4% of Capital Plant	944,000	
General Administrative & Overheads, @ 100% of Labor and Supervision	634,000	
Taxes and Insurance, @ 2% of Capital Plant	472,000	
Depreciation, 10% S.L.	2,361,000	
R.O.I., 25% before taxes on capital plant plus 10% on working capital	<u>6,303,000</u>	
Total Annual Operating Costs		\$17,044,000

III. Operating Costs per ton of ammonia 149.71

Ammonia production costs for both plants as a function of natural gas prices are shown in Figure 28. An important point must be made in conjunction with this comparison. The fuel requirement of the plant producing ammonia from waste carbon monoxide is almost exclusively utilized for steam production. This being the case, coal could be used as fuel at a cost of about $\$1/10^6$ Btu with only a small increase in plant capital costs. The ammonia production cost when using coal for steam generation would be on the order of \$135 per ton and would be competitive with the conventional plant at a natural gas price of about $\$1.88/10^6$ Btu. The fuel requirement of the conventional plant is largely used for reformer heating. Therefore, coal cannot be used for fuel in the conventional plant although fuel oil could be substituted for natural gas.

FIGURE 28. Ammonia Production Costs as a Function of Natural Gas Price

Methanol Production Economics

The process sequence in a conventional methanol plant (ICI low pressure process) utilizing steam reforming of natural gas is:

Primary Reformer. Natural gas is heated together with steam and air in the presence of a catalyst to produce a gas mixture containing CO and hydrogen.

Compression and Synthesis. The gas mixture is compressed (750-1500 psig) and fed to a reactor containing a copper based catalyst at temperatures in the range of 200-300°C.

Methanol Separation. In this step the gas from the synthesis reactor is expanded and cooled. Crude methanol is separated from the unreacted synthesis gas. Conversion of synthesis gas to methanol is relatively low per pass through the synthesis reactor so most of the unreacted synthesis gas is compressed and combined with fresh synthesis gas entering the synthesis reactor. A small stream of unreacted synthesis gas is bled off and used as fuel to prevent the buildup of inert gases in the synthesis reactor.

Methanol Distillation. The crude methanol is separated from low boiling impurities, water and other alcohols in two or more distillation columns.

The methanol from carbon monoxide flowsheet prepared for this study had the following process sequence:

CO Compression. Carbon monoxide, assumed to be available at atmospheric pressure, was compressed to 750 psia.

Shift Conversion. Carbon monoxide was partially converted to hydrogen via the water gas shift reaction to provide a hydrogen to carbon monoxide molecular ratio of two.

Methanol Synthesis. This step was the same as that for a conventional plant.

Methanol Separation and Distillation. These process steps are the same as for a conventional plant except that CO₂ removal was carried out on the recycle synthesis gas stream.

Estimated capital and operating costs for a conventional 1000 tpd methanol plant are shown in Table 62. The estimated production cost for methanol is \$120.36/ton (\$0.40/gal) when natural gas is priced at \$2/10⁶ Btu. Capital and operating cost estimates for a 330 tpd plant producing methanol from carbon monoxide are shown in Table 63. The estimated production cost for methanol from CO is \$92.97/ton (\$0.31/gal) when fuel is priced at \$2/10⁶ Btu. The current market price for methanol is about \$120.00/ton (\$0.40/gallon).

Figure 29 indicates methanol production costs as a function of natural gas prices for both plants. It appears that production of methanol from waste CO is competitive with a conventional methanol plant at a natural gas price of about \$0.82/10⁶ Btu. The plant producing methanol from CO uses fuel for steam production only, so coal or other fuels could be substituted for natural gas.

This preliminary evaluation indicates that methanol production from waste carbon monoxide is much more competitive with conventional technology than is ammonia production. Ammonia production for CO requires an air separation plant or nitrogen purchase, complete conversion of CO to hydrogen via the water-gas shift reaction and consequently a larger carbon dioxide removal requirement. All these factors combine to place ammonia production from waste carbon monoxide at a greater economic disadvantage with conventional technology than is the case with methanol.

In a previous section of this report estimates of the cost of concentrating CO via the COSORB process ranged from \$0.48 to \$0.98/10³ SCF. If concentration of CO is required and the above cost estimates are added to the ammonia production cost shown in Table 61 (\$149.71/ton), the cost of ammonia production is increased to \$181.46/ton and \$214.53/ton, respectively. Similarly, the production cost for methanol, shown in Table 63, is increased from \$0.31/gallon to \$0.42/gallon and \$0.53/gallon by the addition of COSORB costs estimated at \$0.48/10³ SCF and \$0.98/10³ SCF, respectively.

Decreasing supplies of firm natural gas will probably lead to a shift in ammonia and methanol technology from natural gas to heavier petroleum feedstocks in the future. The capital and operating costs for heavy feedstocks are greater than for natural gas based plants. Therefore, the production economics for ammonia and methanol (as well as other chemical commodities) from CO can be expected to become even more attractive in the future.

TABLE 62. Estimated Capital and Operating Costs for
the Production of Methanol from Natural
Gas

Basis: Mid-1976 Gulf Coast estimates for a 1000 ton per day plant operating
330 days per year.

<u>I. Capital Cost</u>	
Capital Plant	36,500,000
Working Capital	7,000,000
<u>II. Operating Costs</u>	
Feedstock, 27.03×10^6 Btu/ton @ \$2.00/ 10^6 Btu	17,840,000
Catalysts and Chemicals	292,000
Utilities:	
Fuel, 5.14×10^6 Btu/ton @ \$2.00/ 10^6 Btu	3,392,000
Electrical Power, @ \$0.02/kWH	31,000
Makeup Water, @ \$0.60/M gal	444,000
Cooling Water Circulation, @ \$0.03/M gal	436,000
Waste Treatment, @ \$0.75/M gal	<u>148,000</u>
	4,451,000
Operating Labor, 26 @ \$22,000/yr (Including benefits)	572,000
Supervision @ 20% of Operating Labor	114,000
Maintenance, @ 4% of Capital Plant	1,460,000
General Administrative & Overheads, @ 100% of Labor and Supervision	686,000
Taxes & Insurance, @ 2% of Capital Plant	730,000
Depreciation, 10% S.L.	3,650,000
R.O.I., 25% before taxes on Capital Plant plus 10% on Working Capital	<u>9,925,000</u>
Total Annual Operating Costs	39,720,000
III. Operating Cost per ton of Methanol	\$120.36
or	\$0.40/gal

TABLE 63. Estimated Capital and Operating Costs For the Production of Methanol from Carbon Monoxide

Basis: Mid-1976 Gulf Coast estimates for a 330 ton per day plant operating 330 days per year.

I. Capital Cost

Capital Plant:

Carbon Monoxide Compression and Shift Conversion	3,223,000
Carbon Dioxide Removal and Steam Generation	2,585,000
Methanol Synthesis, Distillation and Recycle Compression	<u>6,853,000</u>
Total Capital Plant	12,661,000
Working Capital	2,500,000

II. Operating Costs

Feedstock, 890 tons/day CO	--
Catalysts & Chemicals	103,000
Utilities:	
Fuel, @ \$2.00/10 ⁶ Btu	1,988,000
Electrical Power, @ \$0.02/kWh	1,418,000
Makeup Water, @ \$0.60/M gal	195,000
Cooling Water Circulation, @ \$0.03/M gal	139,000
Waste Treatment, @ \$0.75/M gal	<u>49,000</u>
	3,789,000
Operating labor, 15 @ \$22,000/yr (Including benefits)	330,000
Supervision, @ 20% of Operating Labor	66,000
Maintenance, @ 4% of Capital Plant	506,000
General Administrative & Overheads, @100% of Labor and Supervision	356,000
Taxes & Insurance, @ 2% of Capital Plant	253,000
Depreciation, 10% S.L.	1,266,000
R.O.I., 25% before taxes on Capital Plant plus 10% on Working Capital	<u>3,415,000</u>
Total Annual Operating Costs	10,124,000

III. Operating Cost per ton of Methanol	\$92.97
or	\$0.31/gal

FIGURE 29. Methanol Production Costs as a Function of Natural Gas Price

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& \NOVEMBER 5, 1968' &
& BOF >
- 0000117 * APPARATUS FOR RECOVERING WASTE GAS FROM OXYGEN TOP BLOWING
CONVERTER IN UNBURNT STATE &
& \S MAEHARA, I IGARASHI, ET AL' &
& PAT-33377057 \USA' &
& \APRIL 9, 1968' >
- 0000118 * APPARATUS FOR THE REMOVAL OF DUST FROM CONVERTER GASES &
& \H HOFF' &
& PAT-33497194 \USA' &
& \FEBRUARY 24, 1970' &
& BOF STEEL-CONVERTERS >
- 0000119 * METHOD AND APPARATUS FOR THE ANALYSIS OF OFF-GASES IN A
REFINING PROCESS &
& \R FRUMERMAN' &
& PAT-33523657 \USA' &
& \JULY 14, 1970' >
- 0000120 * REMOVAL OF OFF-GASES FROM OXYGEN STEEL CONVERTERS &
& \HP WILLETT' &
& PAT-33592630 \USA' &
& \JULY 13, 1971' >
- 0000121 * OXYGEN-BLOWING LANCE FOR REFINING PIG-IRON TO STEEL AND
BURNING EVOLVED CO IN THE CONVERTER &
& \WE SHEPHERD' &
& PAT-33488044 \USA' &
& \JANUARY 6, 1970' >
- 0000122 * APPARATUS AND METHOD FOR AIR POLLUTION CONTROL COMBINED WITH
SAFE RECOVERY AND CONTROL OF GASES FROM A BOTTOM-BLOWN STEEL
CONVERTER VESSEL &
& \K BAUM, JP BAUM, ET AL' &
& PAT-33908969 \USA' &
& \SEPTEMBER 30, 1975' >
- 0000123 * REGULATING THE COLLECTION WITHOUT COMBUSTION OF GASES FROM THE
PNEUMATIC REFINING OF MELTS &
& \FR ADDN 7 P. ADDN TO FR 1,549,489 CA 71-104354A' &
& PAT-00095774 FRANCE &
& \JUNE 25, 1971' >
- 0000124 * APPARATUS FOR RECOVERY OF CONVERTER GASES &
& \G NAMY' &
& PAT-01316484 FRANCE &
& \FEBRUARY 1, 1963' >
- 0000125 * METHOD FOR CONTROLLING THE TREATMENT OF EXHAUST GASES IN
OXYGEN TOP-BLOWING CONVERTER &
& \Y IWAQ, K NAITO, ET AL' &

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& \AUGUST 1, 1972' >
- 0000126 * WASTE GAS SCREENING IN BASIC OXYGEN PROCESS &
& \D GLASSMAN' &
& \GER OFFEN 12 P.' &
& PAT-02248583 \USA' &
& \APRIL 12, 1973' &
& CARBON-DIOXIDE STEEL PRODUCTION >
- 0000127 * REMOVAL OF CONVERTER GASES &
& \II KAGAN, LB KATSENELENOBOGEN, ET AL' &
& PAT-00438699 USSR &
& \AUGUST 5, 1974' >
- 0000128 * BLOWING OF PIG-IRON &
& \U PUTZIER, D RAOKE, ET AL' &
& PAT-02316768 GERMANY &
& \OCTOBER 17, 1974' >
- 0000129 * COMPLETE OXIDATION OF CO \IN OXYGEN STEELMAKING' &
& \EI NIKOLAENKO, KA GREBEN, ET AL' &
& \PUTI ULUCHSHENIYA PROOLVKI VANNY MARTENOVSK PECHI KISLORODOM
1974, 23-34 RUSS' >
- 0000130 * COMPARISON OF GAS OUTLET CHANNELS OF LARGE-SCALE CONVERTERS
DURING GAS REMOVAL WITH INCOMPLETE COMBUSTION OF CO &
& \LN RAITMAN, AZ RYZHAVSKII, ET AL' &
& \OCHISTKA VOD VOZDUSH BASSEINOV PREDPR CHERN MET 18-22' &
& \1972' &
& WASTE PURIFICATION >
- 0000131 * PROFITS IN EOF GAS COLLECTION &
& \JF SKELLY' &
& \IRON AND STEEL ENG, MARCH 1966, P82-88' >
- 0000132 * GAS COLLECTION WITHOUT COMBUSTION - IRSID-CAFL PROCESS -
OPERATING DATA &
& \C ROEDERER, F MANGIN, ET AL' &
& \J OF METALS, JULY 1966, P852-860' >
- 0000133 * GAS RECOVERY WITHOUT COMBUSTION FROM OXYGEN CONVERTERS - THE
IRSID-CAFL PRESSURE REGULATION PROCESS &
& \G NAMY, J DUMONT-FILLON, ET AL' >
- 0000134 * YAWATAS IMPROVED OG EQUIPMENT AND ITS PERFORMANCE &
& \S MORITA, M NISHIWAKI, ET AL' &
& \J OF METALS, JULY 1966, P861-864' >
- 0000135 * STEAM RECOVERY WITH OXYGEN-BLOWING CONVERTER STACKS \IN FRENCH' &
& \S VIDAL' &
& \TECH MOD 1973, 65, 7-8, 52-6' >
- 0000136 * COMPOSITIONS OF A BLAST FLOW IN THE SUBLANCE ZONE OF AN OXYGEN
CONVERTER &
& \VV YAKOVLEV, SI FILIPPOV, ET AL' &
& \IZV VYSSH UCHES ZAVED, CHERN MET 1973, 3, 23-5 RUSS' >

- 0000137 * PRODUCTION OF ARMCO IRON IN A BASIC ARC ELECTRIC STEEL MELTING FURNACE BY A REVERSE SLAG REGIME AND OXYGEN BLOWING THROUGH THE BATH &
& \A SPASOV, K ERININ, ET AL' &
& \METALURGIYA SOFIA 1973, 3, 1-5 BULG' >
- 0000138 * DISTRIBUTION OF CARBON AND OXYGEN BETWEEN METALLURGICAL AND ENERGY PRODUCTS IN OXYGEN CONVERTER PRODUCTION &
& \T TOSHEV, S DONCHEV' &
& \METALURGIYA SOFIA 1971, 10, 18-21 BULG' >
- 0000139 * INCREASE IN THE EFFECTIVENESS OF AFTERBURNING TECHNOLOGICAL CO OVER AN OPEN-HEARTH FURNACE BATH AT THE DONETS SCIENTIFIC RESEARCH INSTITUTE OF FERROUS METALLURGY \JOINTLY WITH THE KOMMUNARSK METALLURGICAL PLANT' &
& \BS KURAPIN, AK DYMNIKH, ET AL' &
& \STAL 1973, 5, 447A RUSSIAN' >
- 0000140 * REACTION KINETICS IN STEEL PRODUCTION &
& \F OETERS' &
& \TECH MITT 66 8 342' &
& \1973' &
& IRON >
- 0000141 * THE RATE OF DECARBURIZATION OF LIQUID IRON BY CO₂ AND H₂ &
& \RJ FRUEHAN, LJ MARTONIK' &
& \METALLURGICAL TRANS, V5, MAY 1974, P1027-1032' >
- 0000142 * NUCLEATION IN FLUID MEDIA IN STEELWORKS METALLURGY &
& \L VONBOGDANDY, E FOERSTER, ET AL' &
& \KINET METALL PROCESSES STEELMAKING, PROC INT CONF 1970, PUB 1975, 401-16 ENG' >
- 0000143 * PHYSICAL MODEL OF PROCESSES OCCURRING IN THE BATH OF AN OXYGEN CONVERTER &
& \SM SERDYUK, AT KOTSYUBA, ET AL' &
& \AUTOM STALEPLAVILN PROIZVOD 1974, 15-21 RUSS' >
- 0000144 * INTERACTION OF CARBON AND OXYGEN IN MELTS OF IRON, COBALT, AND NICKEL AT DIFFERENT PARTIAL PRESSURES OF CO &
& \VT BURTSEV, VI KASHIN' &
& \STAL 1974, 7, 603-8 RUSS' >
- 0000145 * CINEMATOGGRAPHIC STUDY OF CARBON OXIDATION OF MOLTEN STEEL &
& \VS OKHOTSKII, AG CHERNYATEVICH, ET AL' &
& \IZV VYSSH UCHEB ZAVED, CHERN MET 1973, 5, 24-7 RUSS' >
- 0000146 * KINETICS OF DECARBURIZATION OF LIQUID IRON IN ARGON-CO-CO₂ ATMOSPHERES &
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& \TETSU TO HAGANE 1974, 60, 3, 361-71 JAPAN' >
- 0000147 * EFFECT OF TEMPERATURE AND ALLOYING ELEMENTS ON THE EVOLUTION OF GAS IN LIQUID IRON &
& \H SCHENCK, E STEINMETZ, ET AL' &
& \ARCH EISENHUETTENW 1973, 44, 1, 27-34 GERMAN' >
- 0000148 * CHEMICAL SYNTHESIS METHODS IN FLUID MEDIA IN STEEL-MAKING

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& \L VONBOGDANDY, E FORSTER, ET AL' >

- 0300149 * SAMPLING APPARATUS FOR ANALYZING STEEL CONVERTER EXHAUST GAS &
& \N INOA, A EZAKI, ET AL' &
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& \DECEMBER 19, 1973' >
- 0300150 * RAPIDLY MEASURING CO CONTENT IN A CONVERTER &
& PAT-00795504 BELGIUM &
& \AUGUST 16, 1973' >
- 0000151 * STIRRING OF A STEEL BATH WITH CO BUBBLES &
& \GA DOROFEEV' &
& \PROBL PROIZ-VA CHERN MET 1974, 86-90 RUSS' >
- 0300152 * CO IN STEEL PRODUCTION &
& \D EICKELPASCH' &
& \STAUE-REINHALT LUFT V32, NO 2, FEB 1972, P9-11' >
- 0100153 * STEELMAKING &
& \EC PIORO' &
& PAT-00459516 USSR &
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- 0000154 * STATISTICAL METHOD FOR CONTROLLING THE CONVERSION OF PIG-IRON
IN AN OXYGEN CONVERTER &
& \A PIRKLBAUER, H PINGER' &
& PAT-02459449 GERMANY &
& \JULY 17, 1975' >
- 0300155 * DETAILED STUDY OF CUPOLA EMISSIONS &
& \RD WARDA, RK BUHR' &
& \AFS TRANS, 1973, 81, P32-7' >
- 0000156 * DEVICE FOR THE AFTERBURNING OF CO AND REMOVAL OF DUST OF
WASTE CUPOLA GASES \IN RUSSIAN' &
& \VY BRON, ET AL' &
& \LITEINOE POOIZVOD, 8, 36-37, 1975' >
- 0300157 * ATMOSPHERE OF PLASMA MELTING FURNACES &
& \SZ VASILEV, II MAERGOIZ, ET AL' &
& \TR VSES NAUCH-ISSLED INST ELEKTROTERM OBOURODOVANIYA 1972,
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- 0000158 * CLOSED ELECTRIC FURNACE &
& PAT-02219981 FRANCE &
& \SEPTEMBER 27, 1974' >
- 0300159 * METHOD OF RECOVERING OFF-GAS AND GAS PROBE APPARATUS THEREFOR &
& \DE PIKE' &
& PAT-03186831 \USA' &
& \JUNE 1, 1965' &
& STEEL-FURNACES OXYGEN-CONVERTER ELECTRIC-FURNACES >
- 0000160 * APPARATUS FOR COKING AND COLLECTING THE RESULTING GASES AND THEIR
PRODUCTS &
& \T NICHOLSON' &

- & PAT-00308514 \USA' &
 - & \NOVEMBER 25, 1884' &
 - & FUEL >
- 0000161 * METHOD OF UTILIZING PRODUCTS OF COMBUSTION &
 - & \E BIEDERMANN, EW HARVEY' &
 - & PAT-01451612 \USA' &
 - & \MAY 5, 1891' >
- 0000162 * METHOD FOR RETORTING HYDROCARBONACEOUS SOLIDS &
 - & \J9 JONES, JR., AA REEVES' &
 - & PAT-03941992 \USA' &
 - & \OCTOBER 15, 1974' >
- 0000163 * PURIFICATION OF PETROLEUM COKE &
 - & \WF FRANZ, HV HESS' &
 - & PAT-03595965 \USA' &
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 - & VOLATILE-CARBONYLS >
- 0000164 * CONTINUOUS COKING PROCESS &
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 - & \IRON STEEL ENG 1973, 50, 9, 125-30 ENG' >
- 0000165 * ANNUAL STATISTICAL REPORT, 1975 &
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- 0000166 * COMPILATION OF AIR POLLUTION EMISSION FACTORS, SECOND EDITION &
 - & \EPA, APRIL 1973' >
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 - & PAT-03305312 \USA' &
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 - & REDUCTION-OF-IRON-ORE-WITH-CO MANUFACTURE-OF-AMMONIA >
- 0000168 * US FERRO-ALLOY PLANT POLLUTION STANDARD, US ENVIRONMENTAL PROTECTION AGENCY &
 - & \FED REGIST, 5-4-76, P18498' >
- 0000169 * REACTOR AND METHOD OF MAKING ALUMINUM-SILICON ALLOYS &
 - & \KK SETH, CW LANIER' &
 - & PAT-03661562 \USA' &
 - & \MAY 9, 1972' &
 - & RECYCLE FUEL >
- 0000170 * A PRELIMINARY STUDY OF THE OXIDATION OF ALUMINUM IN CARBON-DIOXIDE AND CO &
 - & \RJ BREAKSPERE' >
- 0000171 * COLLECTING GAS FROM MELT IN AN ELECTROLYTIC ALUMINUM RECOVERY CELL &
 - & \P TORTIL' &
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 - & PAT-02508129 FRANCE &
 - & \SEPTEMBER 4, 1975' &
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- 0000172 * CHROMATOGRAPHIC ANALYSIS OF THE COMPOSITION OF ANODE GAS &
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- 0000173 * REPROCESSING OF ZINC SLAGS IN ELECTRIC FURNACES &
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 & VVP ELYUTIN, YA PAVLOV, ET AL' &
 & IZV VYSSH UCHEB ZAVED CHERN MET 11 5-8' &
 & 1972' &
 & PRODUCTION >
- 0000175 * PROVISION FOR SAFE WORKING CONDITIONS DURING THE SILICIJDING
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 & JUNE 3, 1924' >
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 & VWH WAGGAMAN, HW EASTERWOOD' &
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 & FEBRUARY 5, 1929' >
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 & VHE WHITE' &
 & PAT-01908090 USA' &
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& \MW MURRAY' &
 & PAT-01060206 \USA' &
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 & FUEL >

0000184 * CALCIUM CARBIDE PROCESS &
 & \D EASTMAN' &
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0000187 * PROCESS FOR IMPREGNATION OF LIME WITH CARBON &
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0000188 * PROCESS FOR PRODUCTION OF CARBON BLACK &
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 & CHEMICAL-SYNTHESIS >

0000189 * VAPOR PHASE PRODUCTION OF TITANIUM DIOXIDE PIGMENTS &
 & \WH DUNHAM, JR., CK STODDARD, ET AL' &
 & PAT-03560152 \USA' &
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0000190 * KINETICS OF GASEOUS REDUCTION OF ILMENITE &
 & \JG JONES' &
 & \J APPL CHEM BIOTECHNOL 1975, 25, 8, 561-82 ENG' >

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 & \RH WALSH' &
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 & \SEPTEMBER 27, 1960' &
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0000192 * DETOXICATION OF WASTE GASES FROM SHAFT ELECTRIC CHLORINATION
 FURNACES BY COMBUSTION &
 & \VI BORODIN, GI NOVIKOV, ET AL' &
 & \Sb TR, VSES NAUCH-ISSLEO PROEKT INST TITANA 1972, NO 7-8
 229-36 RUSS' >

0000193 * BIG DUPONT TIO2 PROJECT UNDER WAY AT DELISLE &
 & \CHEMICAL WEEK, SEPT 29, 1976, P11' >

- 0000194 * STATIONARY-ENGINE EXHAUST IS SOURCE OF FERTILIZER &
& \CHEM WEEK, MARCH 3, 1976, P27' >
- 0000195 * REDUCTION OF GYPSUM &
& \NK MEHRA' &
& \INDIAN 15 P.' &
& PAT-00119710 INDIA &
& \MAY 22, 1971' &
& CARBON-DIOXIDE PRODUCTION >
- 0000196 * INCREASING THE RATE OF REACTION IN REDUCING CALCIUM SULFATE TO
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& \U.S. 8 P.' &
& PAT-03640682 &
& \FEBRUARY 8, 1972' &
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- 0000197 * REMOVAL OF PHOSGENE FROM BCL3 &
& \JN HAIMSOHN, LA SMALHEISER, ET AL' &
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- 0000198 * INDUSTRIALLY SIGNIFICANT ORGANIC CHEMICALS PART 3 &
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& \IZV VYSSH UCHEBN ZAVED NEFT GAZ 17 7 67-72' &
& \1974' &
& PRODUCTION CARBON-DIOXIDE BENZENE >
- 0000200 * COMPOSITION OF GASEOUS PRODUCTS OF THE CHLORINATION OF
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& \BE SHENFELD, YN KONSHIN, ET AL' &
& \IZV VYSSH UCHEB ZAVED TSVET MET 14 5 54-7' >
- 0000201 * HYDROCARBON EMISSIONS REDUCTION FROM ETHYLENE DICHLORIDE
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& \DI VORONIN, VF SHISHKIN' &
& \PROM ENERG 1974, 1, 15-17 RUSS' >
- 0000203 * SYNTHESIS OF SODIUM FORMATE FROM AMMONIA PLANT EXHAUST GAS &
& \YY DORFMAN, AM KUNIN' &
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- 0000205 * GASIFICATION OF SPENT SULFITE LIQUOR &
& \KA VEINOV, YY YANYGIN, ET AL' &
& \JUM PROM 1973, 6, 4-6 RUSS' >
- 0000206 * METHOD OF TREATING WASTE SUBSTANCES TO DERIVE HYDROGEN AND OTHER
GASES THEREFROM, AND HYDROGEN-CONTAINING GASEOUS PRODUCT &
& \W JUDA' &
& PAT-03317292 \USA' &
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- 0000207 * COMPOSITION OF GASES FROM HYDROCRACKING OF HIGH-MOLECULAR-WEIGHT
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& \AV RACHINSKII, SM REPYAKH, ET AL' &
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- 0000208 * PRODUCTION OF GAS FOR SYNTHESIS &
& \ET OLSON' &
& PAT-02012477 \USA' &
& \AUGUST 27, 1935' >
- 0000209 * SANITARY-CHEMICAL EVALUATION OF SOME SOFTENERS USED IN
RECLAIMED RUBBER PRODUCTION &
& \BA SHAKHOV, MG VOLKOVA, ET AL' &
& \KOZH-OBUV PROM 1973, 10, 40-2 RUSS' >
- 0000210 * BURNING ISSUE OF PVC DISPOSAL &
& \CA CLARK' &
& \SPE SOC PLAST ENG J 28 7 30-34' &
& \1972' &
& REVIEW HYDROGEN >
- 0000211 * STUDY OF PYROLYTIC PRODUCTS OF POLYMER MATERIALS BY MASS
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& \K HIRAMATSU' &
& \SHITSURYO BUNSEKI 21 4 327-32" &
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- 0000212 * THE PHOTOLYSIS OF POLY\METHYL ACRYLATE' IN VACUUM &
& \L ACKERMAN, WJ MCGILL' &
& \J SOUTH AFRICAN CHEM INST 1973, V26, P92-93' >
- 0000213 * AN EVALUATION OF EMISSIONS AND CONTROL TECHNOLOGIES FOR THE
METAL DECORATING PROCESS &
& \RR GADOMSKI, AV GIMBRONE, ET AL' &
& \J AIR POLLUTION CONTROL ASSOCIATION V24, NO 5, MAY 1974,
P484-490' >
- 0000214 * A SURVEY INTO THE FUMES EVOLVED FROM FOUNDRY SAND BINDERS BASED
ON SYNTHETIC RESINS &
& \RW KAY' >
- 0000215 * ENVIRONMENTAL CONTROL IN THE PLANT OF ALUMINUM SURFACE
TREATMENTS &

- & \K SUZUKI' &
& \HYOMEN SHORI JANARU 1973, 6, 6, 7-14 JAPAN' >
- 0000216 * PURIFICATION OF ACETONE CYANOHYDRIN &
& \Y IIDA, H KATO, ET AL' &
& PAT-73-003824 JAPAN &
& \FEBRUARY 2, 1973' >
- 0000217 * SOME NEW FACTS RELATING TO THE CHEMICAL PROPERTIES OF CO &
& \F LEELAND' &
& \COMPTES RENDUS 1850, 30, 483-485' >
- 0000218 * THE ABSORPTION OF CO BY CUPROUS AMMONIUM CARBONATE AND FORMATE SOLUTIONS &
& \AT LARSON, CS TEITSWORTH' &
& \J OF AMER CHEM SOC, V44, JULY-DEC 1922, P2878-2885' >
- 0000219 * THE ABSORPTION OF CO BY CUPROUS AMMONIUM CARBONATE SOLUTIONS &
& \HR HAINSWORTH, EY TITUS' &
& \J OF AMER CHEM SOC, V43, NO 1, JAN 1921, P1-11' >
- 0000220 * CO FROM BASIC OXYGEN FURNACES &
& \RG MORRISON' &
& \NATURAL RESOURCES RESEARCH INST OR CONTRACT 14-01-0001-1196' &
& \JANUARY 1971' >
- 0000221 * CO REMOVAL. I - COPPER LIQUOR SCRUBBING &
& \HY ALLGOOD' &
& \FERT SCI TECHNOL SER 2, 239-309' &
& \1974' &
& REVIEW AMMONIA SYNTHESIS-GAS PURIFICATION >
- 0000222 * REMOVING CO \FROM SYNTHESIS GAS' BY WASHING WITH COPPER-AMMONIACAL SOLUTIONS &
& \L FODOR' &
& \REV CHIM BUCHAREST 23 2 85-92' &
& \1972' &
& REVIEW SYNTHESIS-GAS PURIFYING >
- 0000223 * ABSORPTION OF CO BY COPPER-AMINE SOLUTIONS &
& \TV VYLIVOK, AS FURMANOV, ET AL' &
& \AZCT PROM-ST 1974, 3, 1-4 RUSS' >
- 0000224 * MISCELLANEOUS GAS-PURIFICATION TECHNIQUES &
& \AL KOHL, FC REISENFELD' &
& \GAS PURIFICATION, P485-533, 1960' >
- 0000225 * PURIFICATION OF GASES FOR AMMONIA MANUFACTURE. REMOVAL OF CO BY CUPRAMMONIUM CARBONATE SOLUTIONS &
& \R EGALON, R VANHILLE, ET AL' &
& \IND AND ENG CHEM, V478 NO 5, MAY 1955, P887-899' >
- 0000226 * THE ABSORPTION OF CO BY SOLUTIONS OF COPPER AMMONIUM SALTS &
& \NM ZHAVOPONKOV, FM RESHCHIKOV' &
& \J CHEM IND USSR 1933 NO 8, 41-49' >
- 0000227 * ABSORPTION OF CO BY CUPRAMMONIUM FORMATE-CARBONATE SOLUTIONS &
& \NM ZHAVOPONKOV, VT CHAGUNAVA' &

& \ZHUR KHIM PROM VOL 17 NO 1 P25-29 1943' >

- 0000228 * PROBLEMS RELATED TO THE LONG-TERM OPERATION OF THE CO REMOVAL
BY COPPER SALT-CONTAINING ALKALINE SOLUTIONS IN AMMONIA
PLANTS \IN HUNGARIAN' &
& \J DEVAY, ET AL' &
& \MAGY KEM LAPJA, 30, P627-632, 1975' >
- 0000229 * RECOVERY OF HIGH CONCENTRATION CO FROM COPPER LIQUOR USED
TO PURIFY AMMONIA SYNTHESIS GAS &
& \R3 MOORE, VT ATKINSON' &
& PAT-03006729 \USA' &
& \OCTOBER 31, 1961' >
- 0000230 * REMOVAL OF CO FROM CONVERTED GAS BY A
CUPRAMMONIUM SOLUTION IN LAMINAR-FLOW APPARATUS OF AMMONIA
PRODUCTION &
& \VM OLEVSKII, AA VINTER, ET AL' &
& \TR NAUCH ISSLEU PROEKT INST AZOTN PROM ORG SIN NO 10 91-111' &
& \1971' >
- 0000231 * HIGH-PURITY CO &
& \T YAMAMOTO' &
& \JAPAN 2 P.' &
& PAT-72-016408 JAPAN &
& \MAY 15, 1972' &
& PURIFICATION >
- 0000232 * HIGHLY PURE CO &
& \T YAMAMOTO' &
& \JAPAN 3 P.' &
& PAT-73-014315 JAPAN &
& \MAY 7, 1973' &
& PURIFICATION >
- 0000233 * HIGH PURITY CO &
& \T YAMAMOTO' &
& \JAPAN 2 P.' &
& PAT-74-034599 JAPAN &
& \SEPTEMBER 14, 1974' &
& PURIFICATION >
- 0000234 * TREATMENTS DURING AMMONIA PRODUCTION &
& \M SVONAVA' &
& \CHEM PROM 21 10 504-6' &
& \1971' &
& SYNTHESIS REMOVAL >
- 0000235 * PROBLEMS RELATED TO THE LONG-TERM OPERATION OF COPPER-LYE
CO REMOVAL UNITS IN AMMONIA PLANTS &
& \J DEVAY, F RATKOVICS, ET AL' &
& \HUNGARIAN J OF IND CHEM VESZPREM V3, P51-70, 1975' >
- 0000236 * THE ABSORPTION OF CO IN AN AQUEOUS SOLUTION OF CUFROUS AMMONIUM
LACTATE IN A PACKED TOWER &
& \WJ THOMAS, SE WATKINS' &
& \J APPL CHEM, 15, JAN 1965, P17-28' >

- 0000237 * ELIMINATION OF CO FROM SYNTHESIS GASES BY ABSORPTION IN
CUPROUS SALT SOLUTIONS &
& \OW VANKREVELEN, CME BAANS' &
& \J OF PHYSICAL + COLLOID CHEM, V54, 1950, P370-390' >
- 0000238 * JOINT SOLUBILITY OF CO AND DIOXIDE IN CUPRAMMONIUM ACETATE -
CARBONATE SOLUTIONS &
& \TV VYLIVOK, AS FURMANOV, ET AL' &
& \J APPL CHEMISTRY, USSR, 47, 1974, P2571-2575' >
- 0000239 * SOLUBILITY OF CO IN CUPRAMMONIUM SOLUTIONS &
& \ZV KORBUTOVA, AS FURMANOV, ET AL' &
& \J APPL CHEMISTRY, USSR, 47, 1974, P2459-2462' >
- 0000240 * PHASE EQUILIBRIA IN THE SYSTEM CUPRAMMONIUM ACETATE SOLUTION -
CO AT A PRESSURE OF 300 KG/CM² &
& \OG IVANOV, OS SHISHKOV' &
& \J OF APPLIED CHEM OF USSR, V37, NO 10, OCT 1964, P2163-2173' >
- 0000241 * THE PARTIAL PRESSURE OF AMMONIA, CARBON-DIOXIDE AND WATER OVER
COPPER AMMONIUM SOLUTIONS &
& \NM ZHAVORONKOV' &
& \J CHEM IND USSR 16 NO 10 36-7 1939' >
- 0000242 * EFFECT OF SOME FACTORS ON THE RATE OF ABSORPTION OF CO BY
COPPER-AMMONIA SOLUTIONS \IN RUSSIAN' &
& \VYLIOK, TV' &
& \TR MOSK KHIM-TEKHNOL INST, 79, P78-80, 1974' >
- 0000243 * SOLUBILITY OF CO IN COPPER-AMINE ACETATE-CARBONATE SOLUTIONS &
& \TV VYLIVOK, AS FURMANOV, ET AL' &
& \TR MOSK KHIM-TEKHNOL INST 1974, 79, 81-3 RUSS' >
- 0000244 * MASS TRANSFER COEFFICIENT IN A PACKED ABSORBER DURING
ABSORPTION OF CO BY A CUPRAMMONIUM SOLUTION &
& \NV KSANDROV, GM STRONGIN' &
& \TR KHIM KHIM TEKHNOL 1973, 4, 15-16 RUSS' >
- 0000245 * CALCULATION OF THE COEFFICIENT OF MASS TRANSFER IN A
PACKED CUPRAMMONIUM ABSORBER &
& \NV KSANDROV, ZV KORBUTOVA, ET AL' &
& \IZV VYSSH UCHEB ZAVED KHIM KHIM TEKHNOL 1973, 16, 9,
1431-5 RUSS' >
- 0000246 * CONTINUOUS DETERMINATION OF AMMONIA ACTIVITY IN AMMONIACAL
SOLUTIONS &
& \EH BROWN, JE CLINE, ET AL' &
& \IND AND ENG CHEM, VOL 17, NO 5, MAY 1945, P280-282' >
- 0000247 * BINARY COPPER CARBONYLS. SYNTHESIS AND CHARACTERIZATION OF
Cu₂CO₃, Cu₂CO₂, CuCO, AND Cu₂CO₆ &
& \H HUBER, EP KUNDIG, ET AL' &
& \J AM CHEM SOC, 1975, 97, 8, P2097-106' >
- 0000248 * THE SULZER CO REMOVAL PROCESS &
& \A MEYER' &
& \COKE AND GAS, MARCH 1961, P107-111' >

- 0000249 * A TOWN GAS DETOXIFICATION PLANT AT WINTERTHUR &
& \A MEYER' >
- 0000250 * CO REMOVAL FROM TETRAFLUOROETHYLENE &
& \S YOSHIDA, K TAMASHIMA' &
& PAT-71-000004 JAPAN &
& \JANUARY 5, 1971' >
- 0000251 * COMBINED REMOVAL OF CARBON-DIOXIDE AND CO CONTAINED IN THE
GASEOUS MIXTURES FROM AMMONIA SYNTHESIS &
& PAT-00810645 ITALY &
& \JANUARY 15, 1968' >
- 0000252 * WINNING COPPER USING CO &
& \M DUBECK, SJ IM' &
& PAT-03918962 \USA' &
& \NOVEMBER 11, 1975' >
- 0000253 * METAL RECOVERY FROM AMMONIACAL SOLUTIONS &
& \BRIT 6 P.' &
& PAT-01252065 \USA' &
& \NOVEMBER 3, 1971' &
& CARBONYL PRODUCTION >
- 0000254 * COMPLEXING LIGANDS WITH A FLUIDIZED BED OF CUPROUS CHLORIDE &
& \WH SAWYER, RE LONG, ET AL' &
& PAT-03441377 \USA' &
& \APRIL 29, 1969' &
& RECOVERY BUTADIENE >
- 0000255 * REMOVAL OF COPPER FROM WASTE WATER WITH ION EXCHANGE RESINS &
& \GE BAISERO, A CALLEGARO, ET AL' &
& \INQUINAMENTO 1973, 15, 5, 37-9 SPAN' >
- 0000256 * RECOVERY OF CO BY MEANS OF CUPROUS CHLORIDE IN PROPIONITRILE &
& \GC BLYTAS, ER BELL' &
& PAT-03415615 \USA' &
& \DECEMBER 10, 1968' &
& COPPER-LIQUOR RECOVERY >
- 0000257 * AROMATICS RECOVERY WITH CO CUPROUS FLUOROBORATE AND CO
CUPROUS FLUOROPHOSPHATE COMPLEXES &
& \HJ GEBHART, JR., EC MAKIN, JR., ET AL' &
& PAT-03578581 \USA' &
& \MAY 11, 1971' >
- 0000258 * CO AS A FUEL &
& \DG WALKER' &
& \AM CHEM SOC, DIV FUEL CHEM, PREPR 1973, 18, 3, 78-83 ENG' >
- 0000259 * COSORE - A PROCESS FOR THE RECOVERY OF CO &
& \DJ HAASE, DG WALKER' &
& \TENNECO CHEMICALS, INC' &
& \PAPER PRESENTED AT 4TH JOINT CHEMICAL ENGINEERING CONF,
VANCOUVER, B.C., CANADA, SEPTEMBER 9-12, 1973' >
- 0000260 * NEW SOLVENT CUTS COSTS OF CO RECOVERY &
& \DJ HAASE' &

& \REPRINT FROM CHEMICAL ENGINEERING, AUGUST 4, 1975' >

- 0000261 * REMOVAL OF CO FROM GASEOUS MIXTURES BY COMPLEXATION &
& \RG TURNBO, DA KEYWORTH' &
& PAT-0241480 GERMANY &
& \OCTOBER 17, 1974' >
- 0000262 * MAKING AND USING CO &
& \OG WALKER' &
& \CHEMTECH MAY 1975, P308-311' >
- 0000263 * THE COSORB PROCESS &
& \OJ HAASE, OG WALKER' &
& \CHEM ENG PROGRESS, VOL 70, NO 5, MAY 1974, P74-77' >
- 0000264 * TENNECO CHEMICALS BELGIUM HAS RELEASED DETAILS OF ITS NEW
COSORB PROCESS &
& \EUR CHEM N 73-04-20 P30' >
- 0000265 * KTI REACHES AGREEMENT WITH TENNECO &
& \EUR CHEM N 74-04-12 P23' >
- 0000266 * RECOVERY OF CO BY NONCRYOGENIC METHODS &
& \EUR CHEM N 75-07-18 P23' >
- 0000267 * FEASIBILITY OF SEPARATING CO FROM PRODUCER GAS &
& \RA FISHER, MK BUDER, ET AL' &
& \PS-245653 122 P.' &
& \SEPTEMBER 1975' >
- 0000268 * SEPARATION OF IMPURITIES FROM GASES &
& \RG TURNBO, DA KEYWORTH' &
& \GER OFFEN 20 P.' &
& PAT-02444211 \U.S.' &
& \APRIL 3, 1975' &
& PURIFICATION COPPER >
- 0000269 * COPPER ALUMINUM COMPLEX &
& \RG TURNBO' &
& PAT-02414801 GERMANY &
& \OCTOBER 17, 1974' >
- 0000270 * NEWS-ITEM UNION MAKES ITS PITCH &
& \CHEM-CAL WEEK, SEPT 5, 1973, V113, P13' >
- 0000271 * TENNECO GRANTS DOW FIRST COSORB LICENSE FOR CO &
& \CHEM MARKETING REPORT, JULY 21, 1975' >
- 0000272 * ACETYLENE, CO, DOW CHEMICAL CO, TENNECO COSORB PROCESS, TOLUENE
DIISOCYANATE &
& \NITROGEN SEPT/OCT, 1975, P42' >
- 0000273 * CO, CHEMICAL ABSORPTION, COSORB CHEMICAL ABSORPTION PROCESS,
DOW CHEMICAL CO, TENNECO CHEMICALS INC &
& \CHEM ENG, NY, 7-21-75, P52' >
- 0000274 * ACETYLENE, CO, COSORB CHEMICAL ABSORPTION PROCESS, DOW CHEMICAL CO,
TENNECO CHEMICALS INC, TOLYLENE DIISOCYANATE &

- & \CHEM WEEK, 7-16-75, P13' >
- 0000275 * CO, COSORB PROCESS, DOW CHEMICAL USA, TENNECO CHEMICALS INC &
& \CHEM MARK REP, 7-21-75, P3' >
- 0000276 * KTI ACQUIRES LICENSE FOR TENNECO COSORB PROCESS &
& \A MORE' &
& \NITROGEN, JULY/AUGUST 1974, 90, P12-14' >
- 0000277 * RECOVERY OF GROUP IB METAL HALIDES FROM BIMETALLIC SALT
COMPLEXES &
& \OG WALKER, DJ HAASE, ET AL' &
& \U.S. 3 P.' &
& \PAT-43845188 &
& \OCTOBER 29, 1974' &
& \REMOVAL HYDROCARBON ACETYLENE PURIFICATION >
- 0000278 * TRENDS IN CRYOGENIC GAS SEPARATION AND LIQUEFACTION PLANTS &
& \S SAITO, A NUMATA' &
& \CHEM ECON ENG REV 6 12 10-21' &
& \1974' &
& \REVIEW HYDROGEN ETHYLENE >
- 0000279 * CO REMOVAL. III - LOW-TEMPERATURE PURIFICATION &
& \HC FOWLES' &
& \FERT SCI TECHNOL SER 2, 321-32' &
& \1974' &
& \REVIEW AMMONIA SYNTHESIS-GAS >
- 0000280 * LOW-TEMPERATURE PROCESSES FOR PURIFYING HYDROGEN AND
CO FEEDSTOCKS FOR INDUSTRIAL CHEMICAL PRODUCTS &
& \H TANZ' &
& \PROGR REFRIG SCI TECHNOL PROC INT CONGR REFRIG 13TH 1 619-25' &
& \1973' &
& \CRYOGENIC PURIFICATION CARBON-DIOXIDE REMOVAL >
- 0000281 * LOW-TEMPERATURE PROCESSES &
& \OF BAKER' &
& \CHEM ENG PROGRESS, V51, NO 9, SEP 1955, P399-402' >
- 0000282 * RECOVERY WITHOUT COMBUSTION OF THE GAS OBTAINED DURING THE
PREPARATION OF PURE OXYGEN \IN FRENCH' &
& \M ALLARD, G NAMY' &
& \REVUE DE METALLURGIE, MARCH 1960, V57, P207, 220' >
- 0000283 * HYDROGEN RECOVERY BY CRYOGENIC SEPARATION &
& \A NUMATA' &
& \CHEM ECONOMY + ENG REVIEW, NOV 1970, P15-22' >
- 0000284 * PRACTICAL APPLICATION EXAMPLES FOR THE PURIFICATION AND
SEPARATION OF GASES \IN GERMAN' &
& \M REICHEL' &
& \TECH MITT, 63, 6, JUNE 1970, P267-272' >
- 0000285 * CRYOGENIC SEPARATION AND ABSORPTION APPLIED IN GAS PURIFICATION
AND ESPECIALLY IN HYDROGEN PRODUCTION &
& \M OUCOURANT' &
& \CHIM IND GENIE CHIM 104 21 2677-81' \IN FRENCH' &

& \1971' >

- 0000286 * CO FROM CRUDE GAS OF A STEAM-REFORMING PLANT &
& \RJ ALLAM, BR BLIGH' &
& PAT-02323410 &
& \NOVEMBER 29, 1973, 20 P' >
- 0000287 * HOT REDUCING GASES &
& PAT-00794490 BELGIUM &
& \JULY 24, 1973' >
- 0000288 * LIQUEFACTION FOR SEPARATING HYDROGEN FROM COKE-OVEN GAS &
& \P GUILLAUMERON' &
& \CHEM ENG, JULY 1949, V56, NO 7, P105-110' >
- 0000289 * PRODUCING AMMONIA SYNTHESIS GAS &
& \JS BARDIN, DW BEERY' &
& \PETROLEUM REFINER, V32, NO 2, FEB 1953, P99-102' >
- 0000290 * GAS-LIQUID EQUILIBRIUMS CARBON-DIOXIDE-CO AND
CARBON-DIOXIDE-METHANE-CO SYSTEMS &
& \LJ CHRISTIANSEN, A FREDENSLUND, ET AL' &
& \ADV CRYOG ENG 19 309-19' &
& \1974' &
& METHANE >
- 0000291 * PHASE EQUILIBRIUM PROBLEMS IN THE SEPARATION OF DIHYDROGEN
SULFIDE, CARBON-DIOXIDE, AND CO FROM NATURAL GAS
MIXTURES &
& \LJ CHRISTIANSEN' &
& \INT SCAND CONGR CHEM ENG PROC A VII. 1-12' &
& \1974' &
& REVIEW PURIFICATION HYDROGEN-SULFIDE >
- 0000292 * SEPARATION AND RECOVERY OF CO &
& \K ICHIHARA' &
& PAT-70-003650 JAPAN &
& \FEBRUARY 6, 1970' >
- 0000293 * WASHING OUT OF CO BY MEANS OF LIQUID NITROGEN &
& \II GELPERIN, LL RAPOPORT' &
& \TRUDY GOSUDARST NAUCH-ISSLEDOVATEL I PROEKT INST AZOT PROM
1956, NO. 5, 249-60' >
- 0000294 * GAS-MIXTURE FRACTIONATION &
& \D DOMINE, L HAY' &
& PAT-01946196 GERMANY &
& \APRIL 16, 1970' >
- 0000295 * REPROCESSING OF GASES CONTAINING CO AND HYDROGEN &
& \VI KUCHERYAVYI, DM GORLOVSKII, ET AL' &
& PAT-00346302 USSR &
& \JULY 28, 1972' >
- 0000296 * SEPARATION OF THE COMPONENTS OF REFINERY TAIL GAS &
& PAT-01068982 U.K. &
& \MAY 17, 1967' >

- 0000297 * CONTINUOUS SEPARATION OF GAS MIXTURES HAVING AT LEAST THREE
COMPONENTS BY SOLVENT EXTRACTION &
& \G NATTA' &
& PAT-06489556 ITALY &
& \JANUARY 23, 1954' >
- 0000298 * SEPARATING GASES SUCH AS HYDROGEN FROM CO AND NITROGEN &
& \P SCHUFTAN' &
& PAT-01773012 \USA' >
- 0000299 * PROCESS FOR THE SEPARATION OF GAS MIXTURES &
& \P SCHUFTAN' &
& PAT-01773012 GERMANY &
& \JULY 27, 1927' >
- 0000300 * METHODS FOR SEPARATING MIXTURES OF NORMALLY GASEOUS MATERIALS &
& \JA PRYOR' &
& PAT-03319429 \USA' &
& \NOVEMBER 22, 1965' >
- 0000301 * GAS SEPARATION PROCESS AND APPARATUS &
& \F JAKOB' &
& PAT-03251189 GERMANY &
& \APRIL 12, 1961' >
- 0000302 * CO REMOVAL. II - METHANATION &
& \JR PHILLIPS' &
& \FERT SCI TECHNOL SER 2, 311-19' &
& \1 74' &
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CARBON-DIOXIDE >
- 0000303 * PROCESS FOR THE REMOVAL OF CO FROM MIXTURES THEREOF WITH
HYDROGEN &
& \K ERDMANN' &
& PAT-02254799 &
& \APRIL 22, 1939' >
- 0000304 * PURIFYING GAS MIXTURES CONTAINING PARTICULARLY CO
AS IMPURITY &
& \L HAY' &
& \CAN 12 P.' &
& PAT-06953657 FRANCE &
& \AUGUST 27, 1974' &
& REMOVAL WASTE >
- 0000305 * APPARATUS FOR REMOVING CO FROM THE AIR BY ADSORPTION &
& \F TATAI' &
& PAT-74-086272 JAPAN &
& \AUGUST 19, 1974' >
- 0000306 * THE INHIBITION BY NITROGEN OF THE CHEMISORPTION OF CO ON AN
UNPROMOTED IRON CATALYST &
& \YY HUANG, PH EMMETT' &
& \J OF CATALYSIS 24, P101-105, 1972' >
- 0000307 * CONCENTRATION OF THE CO IMPURITY FROM GASEOUS
MIXTURES &

& \EE SOTNIKOV, GA GAZIEV' &
 & \PROTSESSY KHROMATOGR KOLONKAKH 17 29-31' &
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 & CHROMATOGRAPHIC >

- 000308 * THE EVALUATION OF GAS DETECTOR TUBE SYSTEMS - I. CO &
 & \AS MORGENSTERN, RM ASH, ET AL' &
 & \AM IND HYGIENE ASSOC J, 31, 5, 630-632, SEPT-OCT 1973' >
- 000309 * PURIFYING GAS MIXTURES &
 & \GV TSITSISHVILI, TG ANDRONIKASHVILI, ET AL' &
 & PAT-00483993 USSR &
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- 000310 * GAS SEPARATION BY SELECTIVE ADSORPTION &
 & \ECR SPOONER' &
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- 000311 * RECOVERY OF CO AND HYDROGEN FROM HIGH NITROGEN CONTENT GAS &
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- 000312 * IRON-GROUP IMPREGNATED ADSORBENT IN ADSORPTION PROCESS &
 & \CHO BERG, HC REED, ET AL' &
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 & PRODUCEP-GAS-SEPARATION IRON-ADSORPTION >
- 000313 * DIFFUSION SEPARATION APPARATUS FOR GASES \IN GERMAN' &
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 & \Z NATURFORSCH 6A, 213-217, 1951' >
- 000314 * ON THERMAL DIFFUSION \IN GERMAN' &
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 & \ZTSCHR ELEKTROCHEM, 80 46, NR 3, 1940, P203-212' >
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- 000317 * SEPARATION OF BINARY MIXTURES OF CO AND H2 BY PERMEATION THROUGH
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 & \FP MCCANDLESS' &
 & \IND ENG CHEM PROCESS DES DEVELOP., VOL 11, NO 4, 1972,
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- 000318 * SEPARATING MIXTURES OF GASES &
 & \WJ WARD' &

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& \Y MATSUSHIMA, T KOYANO, ET AL' &
& PAT-75-122499 JAPAN &
& \SEPTEMBER 26, 1975' >
- 0000320 * ABSORPTION OF CO BY SILVER COMPOUNDS &
& \Y SOUMA, H SANO' &
& \CHEM LETT 1973, 10, 1059-60 ENG' >
- 0000321 * PROCESS OF CONCENTRATING OR PURIFYING CO OCCURRING IN
ADMIXTURE WITH OTHER GASES &
& \KM WATSON' &
& PAT-C2593232 \USA' &
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- 0000322 * PREPARATION AND REACTIONS OF A TITANIUM \IV' METALLOCYCLE.
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& \JX MCDOERMOTT, GM WHITESIDES' &
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REACTIONS WITH HYDROGEN, NITROGEN, AND CO &
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- 0000324 * REVERSIBLE ADDITION OF CO TO TETRACARBONYLBIS
\ETA5-PENTAMETHYLCYCLOPENTADIENYL' - DIMOLYBDENUM \I' &
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- 0000325 * MOLYBDENUM COMPLEXES AS CATALYSTS FOR THE REDUCTION OF MOLECULAR
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& \AE SHILOV, AK SHILOVA, ET AL' &
& \REACTION KINETICS + CATALYSIS LETTERS, V3, NO2,
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- 0000326 * PHOSPHINE NICKEL \II' BIS \DIETHYLSELENOCARBAMATE', L2NI
\SEC 0 NET2*2 L2 EQUALS 2 TRIPHENYLPHOSPHINE, 1.2 -
BIS \DIPHENYLPHOSPHINO' ETHENE. PREPARATION AND REACTION WITH
CO &
& \K TANAKA, T TANAKA' &
& \INORG NUCL CHEM LETT 20 7 605-8' &
& \1974' &
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- 0000327 * BIS \DIPHENYLGLYOXIMATE' - DIPYRIDINE - IRON \II' AND RELATED
SPIN-PAIRED D6 COMPLEXES. PREPARATION, PROPERTIES, AND REACTIONS
WITH CO, MOLECULAR OXYGEN, AND OTHER COVALENT
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& \T YAMAJI' &
& \245 P.' &
& \1972' >

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& \WE NEWTON, JE SEARLES' &
& \INORG CHIM ACTA 7 3 349-52' &
& \1973' &
& HALIDE CARBONYL PHOSPHINE >
- 0000329 * RHODIUM \I' - AMINE COMPLEXES. I - CHLOROMONOAMINE - 1.5 - CYCLOOCTADIENERHODIUM \I' TYPE COMPLEXES AND THEIR REACTION PRODUCTS WITH CO &
& \P FOUGEROUX, B DENISE, ET AL' &
& \J ORGANOMETAL CHEM 60 2 375-86' &
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- 0000330 * AMINE COMPLEXES OF RHODIUM \I'. II - \RHCOOL₂ PLUS L EQUALS PYRIDINES AND COO EQUALS 1.5-CYCLOOCTADIENE' CATIONIC COMPLEXES AND THEIR REACTION PRODUCTS WITH CO &
& \J DENISE, G PANNETIER' &
& \J ORGANOMETAL CHEM 63 423-30' &
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- 0000331 * LOW OXIDATION STATES RUTHENIUM CHEMISTRY. I - REACTIONS OF DICHLOROTRIS\TRIPHENYLPHOSPHINE' RUTHENIUM AND RELATED COMPLEXES WITH SMALL MOLECULES &
& \S CENINI, A MANTOVANI, ET AL' &
& \GAZZ CHIM ITAL 1975, 105, 3-4, 255-73 ENG' >
- 0000332 * BINDING AND ACTIVATION OF ENZYMIC SUBSTRATES BY METAL COMPLEXES. III - REACTIONS OF MO\CO'₂ \S₂CN/C₂H₅/2'₂ &
& \JW McDONALD, WE NEWTON, ET AL' &
& \J OF ORGANOMETALLIC CHEM, 92, 1975, P-C25-C27' >
- 0000333 * REACTIONS OF BIS \TRIETHYLPHOSPHINE' TITANIUM \III' CHLORIDE WITH SMALL GASEOUS MOLECULES \ABSTRACT' &
& \TA BALLINTINE' &
& \DISS ABSTR INT B 1975, 35, 12, PT 1' >
- 0000334 * ACTIVITY OF A NEW POLYOXIME-COPPER COMPLEX IN THE REVERSIBLE UPTAKE OF MOLECULAR OXYGEN AND CO IN THE POLYMERIZATION OF ACRYLONITRILE, AND IN THE ADDITION REACTION OF ALCOHOLS TO ACROLEIN &
& \SJ KIM, T TAKIZAWA' &
& \MAKROMOL CHEM 1975, 176, 4, 891-903 ENG' >
- 0000335 * REVERSIBLE UPTAKE OF MOLECULAR OXYGEN AND CO BY A NEW POLYOXIME - COPPER COMPLEX &
& \SJ KIM, T TAKIZAWA' &
& \J CHEM SOC CHEM COMMUN 1974, 9, 356-7 ENG' >
- 0000336 * PREPARATION OF A NOVEL POLYOXIME AND REVERSIBLE UPTAKES OF MOLECULAR OXYGEN AND CO BY ITS METAL COMPLEXES &
& \SJ KIM, T TAKIZAWA' &
& \MAKROMOL CHEM 175 1 125-36' &
& \1974' &
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- 0000337 * PROCESS OF PRODUCING GASES FOR THE MANUFACTURE OF OXYGENATED ORGANIC COMPOUNDS &

- & \M PIER, M MULLER-CUNRADI, ET AL' &
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 & \OCTOBER 16, 1973' >
- 0000451 * METHANIZATION OF CO AND CARBON-DIOXIDE CONTAINING GASEOUS MIXTURES &
 & \A SCHOENMEIER, W LAUSCH, ET AL' &
 & PAT-00097650 EAST GERMANY &
 & \MAY 12, 1973' >
- 0000452 * HYDROCARBONS BY THE FISCHER-TROPSCH METHOD &
 & \MA VANNICE, RL GARTEN' &
 & PAT-02457417 GERMANY &
 & \JUNE 19, 1975' >
- 0000453 * CATALYTIC SYNTHESIS OF HYDROCARBONS FROM HYDROGEN-CO
 MIXTURES OVER THE GROUP VIII METALS. I - SPECIFIC ACTIVITIES
 AND PRODUCT DISTRIBUTIONS OF SUPPORTED METALS &
 & \MA VANNICE' &
 & \J CATAL 37 3 449-61' &
 & \1975' &
 & METHANATION >
- 0000454 * THE CATALYTIC SYNTHESIS OF HYDROCARBONS FROM H2/CO MIXTURES
 OVER THE GROUP VIII METALS. II - THE KINETICS OF THE
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 & \MA VANNICE' &
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- 0000455 * CATALYTIC SYNTHESIS OF HYDROCARBONS FROM MOLECULAR
 HYDROGEN/CO MIXTURES OVER THE GROUP VIII METALS.
 III - METAL-SUPPORT EFFECTS WITH PLATINUM AND PALLADIUM CATALYSTS &

- & \MA VANNICE' &
 & \J CATAL 40 1 129-34' &
 & \1975' &
 & METHANE PREPARATION >
- 0000456 * ON THE SYNTHESIS OF POLYMETHYLENE FROM CO AND HYDROGEN &
 & \H PICHLER, F BELLSTEDT' &
 & \ERDOL UND KOHLE, 26, 10, 560-564, 1973' >
- 0000457 * CATALYST FOR SYNTHESIS OF HYDROCARBONS FROM CO
 AND HYDROGEN &
 & \YT EIDUS, AL LAPIDUS, ET AL' &
 & \U.S.S.R.' &
 & PAT-004886, 7 &
 & \OCTOBER 25, 1975' &
 & PREPARATION >
- 0000458 * INTEGRATED PROCESS FOR PRODUCING C2 HYDROCARBONS FROM CO AND
 HYDROGEN &
 & \CM STARKS' &
 & PAT-03932552 \USA' &
 & \JANUARY 13, 1976' >
- 0000459 * SYNTHETIC GASOLINE &
 & \F BANDIN' &
 & PAT-00800475 BELGIUM &
 & \MARCH 29, 1974' >
- 0000460 * DEVELOPMENT STUDIES ON CONVERSION OF METHANOL AND RELATED
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 & \SE VOLTZ, JJ WISE' &
 & \FE-1773-11, ERDA, OCTOBER 1975' &
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- 0000462 * DEVELOPMENT STUDIES ON CONVERSION OF METHANOL AND RELATED
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 & \SE VOLTZ, JJ WISE' &
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- 0000463 * ADSORPTION OF CO AND HYDROGEN ON \IRON' FISCHER-TROPSCH CATALYSTS &
 & \PN MUKHERJEE, NC GANGULI, ET AL' &
 & \INDIAN J TECHNOL, V3, JANUARY 1965, P15-18' >
- 0000464 * METAL CLUSTERS IN CATALYSIS. IV - CATALYTIC HYDROGEN REDUCTION
 OF CO TO ALKANES &
 & \MG THOMAS, BF BEIER, ET AL' &
 & \J AM CHEM SOC 1976, 98, 5, 1296-7 ENG' >
- 0000465 * DESIGN OF CATALYTIC SYSTEMS FOR HYDROCARBON SYNTHESIS. I -

- SYNTHESIS OF NORMAL ALKANES BY HYDROGENATING CO WITHOUT PRESSURE &
 & \YL POLYAKIN' &
 & \VOPR KINETIKI KATALIZA 1973, 1, 115-18 RUSS' >
- 0000466 * PARTIAL OXIDATION OF METHANE IN A MOTORED ENGINE &
 & \PE OBERDORFER, JR' &
 & PAT-02922849 \USA' &
 & \JANUARY 26, 1960' &
 & METHANOL FORMALDEHYDE >
- 0000467 * SYNTHETIC METHANOL PROCESS &
 & \WJ EDMONDS' &
 & PAT-01975714 \USA' &
 & \SEPTEMBER 6, 1932' &
 & CARBON-DIOXIDE HYDROGEN >
- 0000468 * PROCESS FOR SYNTHESIZING METHANOL &
 & \RL BROWN' &
 & PAT-02281228 \USA' &
 & \APRIL 28, 1942' >
- 0000469 * SYNTHETIC MANUFACTURE OF METHANOL &
 & \A MITTASCH, M PIER' &
 & PAT-01569775 \USA' &
 & \JANUARY 12, 1926' &
 & PRODUCTION COMPLETE-EXCLUSION-OF-IRON >
- 0000470 * PRODUCTION OF ALCOHOLS &
 & \E PEUKERT, F HILBERATH' &
 & PAT-02621202 \USA' &
 & \DECEMBER 9, 1952' &
 & METHANOL IRON-CARBONYL-FORMATION >
- 0000471 * PROCESS FOR THE REGENERATION OF CATALYSTS &
 & \RL BROWN' &
 & PAT-02276921 \USA' &
 & \MARCH 17, 1942' &
 & IRON NICKEL COBALT METHANOL-SYNTHESIS >
- 0000472 * PRODUCTION OF FORMALDEHYDE &
 & \U GERLOFF, J JAHN, ET AL' &
 & PAT-03318955 \USA' &
 & \MAY 9, 1957' &
 & FORMALDEHYDE-SYNTHESIS METHANOL IRON PENTACARBONYL >
- 0000473 * SYNTHETIC METHANOL PROCESS &
 & \LA STENGEL' &
 & PAT-01754371 \USA' &
 & \APRIL 15, 1930' &
 & METHANOL-SCRUBBING >
- 0000474 * PROCESS FOR INCREASING PERMANGANATE TIME OF METHANOL &
 & \AH CONRAD, JR., WG COPPER, ET AL' &
 & PAT-03526670 \USA' &
 & \SEPTEMBER 1, 1971' &
 & PURIFICATION >
- 0000475 * METHANOL REFINING &

& \RB AKELL' &
 & PAT-03391064 \USA' &
 & \JULY 2, 1968' >

0000476 * MANUFACTURE OF OXYGENATED ORGANIC COMPOUNDS &
 & \A MITTASCH, M PIER, ET AL' &
 & PAT-01791568 \USA' &
 & \FEBRUARY 10, 1931' &
 & METHANOL PRODUCTION HYDROGEN >

0000477 * MANUFACTURE OF ORGANIC COMPOUNDS CONTAINING OXYGEN &
 & \M PIER, G WIETZEL' &
 & PAT-01788170 \USA' &
 & \JANUARY 6, 1931' &
 & METHANOL PRODUCTION DILUTE INERT-GAS-ADDITION >

0000478 * DIFFUSION REACTION &
 & \H WALTER' &
 & PAT-01685759 \USA' &
 & \SEPTEMBER 25, 1928' &
 & METHANOL PRODUCTION CCOUNTERCURRENT-DIFFUSION >

0000479 * SYNTHETIC PRODUCTION OF BODIES FROM THEIR COMPONENT GASES &
 & \RS RICHARDSON' &
 & PAT-01704214 \USA' &
 & \MARCH 5, 1929' &
 & METHANOL AMMONIA PRODUCTION REACTOR-TEMPERATURE-CONTROL >

0000480 * PROCESS OF PRODUCING REDUCTION PRODUCTS OF CARBON-DIOXIDE &
 & \AO JAEGER' &
 & PAT-01735925 \USA' &
 & \NOVEMBER 19, 1929' &
 & METHANOL MULTI-STAGE-REACTOR >

0000481 * SYNTHETIC METHANOL PROCESS &
 & \WJ EDMONDS, LA STENGEL' &
 & PAT-01797569 \USA' &
 & \MARCH 24, 1931' &
 & PRODUCTION >

0000482 * CATALYTIC APPARATUS &
 & \WJ EDMONDS' &
 & PAT-01848466 \USA' &
 & \MARCH 8, 1932' &
 & PRODUCTION METHANOL >

0000483 * SYNTHETIC PRODUCTION OF METHANOL &
 & \RS RICHARDSON' &
 & PAT-01921776 \USA' &
 & \AUGUST 8, 1933' &
 & TEMPERATURE-CONTROL-IN-REACTOR >

0000484 * PROCESS AND APPARATUS FOR CARRYING OUT EXOTHERMIC CHEMICAL
 REACTIONS &
 & \LA STENGEL' &
 & PAT-02512586 \USA' &
 & \JUNE 20, 1950' &
 & METHANOL-SYNTHESIS GAS-RECYCLE >

- 0000485 * CATALYTIC REACTOR &
& \HGEL DERYCKER, ET AL' &
& PAT-02887365 \USA' &
& \MAY 19, 1959' &
& METHANOL-SYNTHESIS >
- 0000486 * MULTIPLE BED CATALYST APPARATUS HAVING CLOSE TEMPERATURE CONTROL &
& \TO WENTWORTH' &
& PAT-03254967 \USA' &
& \JUNE 7, 1966' &
& METHANOL AMMONIA-SYNTHESIS >
- 0000487 * PROCESS AND APPARATUS FOR PERFORMING REACTIONS IN THE GASEOUS
PHASE &
& \HJ HANSEN' &
& PAT-03372988 \USA' &
& \MARCH 12, 1968' &
& AMMONIA METHANOL >
- 0000488 * CATALYTIC CONVERTER &
& \PP KING, JR POTTER' &
& PAT-03458289 \USA' &
& \JULY 29, 1969' &
& METHANOL AMMONIA-SYNTHESIS >
- 0000489 * MULTIPLE ZONE APPARATUS FOR THE PROCESSING OF FLUIDS HAVING
INTERZONE FLUID MIXING AND REDISTRIBUTION FEATURES &
& \TO WENTWORTH, CG ANDERSON' &
& PAT-03483407 \USA' &
& \NOVEMBER 25, 1969' &
& GAS-PHASE MULTI-ZONE-CATALYTIC-REACTOR METHANOL-SYNTHESIS >
- 0000490 * PROCESS FOR CARRYING OUT CYCLIC SYNTHESIS REACTIONS AT
ELEVATED PRESSURES &
& \JA FINNERAN, MC MAYO' &
& PAT-03484197 \USA' &
& \DECEMBER 16, 1969' &
& METHANOL AMMONIA >
- 0000491 * LOW PRESSURE-DROP CATALYTIC REACTOR &
& \R FAWCETT, AW SMITH, ET AL' &
& PAT-03694169 \USA' &
& \SEPTEMBER 26, 1972' &
& METHANOL AMMONIA-SYNTHESIS >
- 0000492 * METHANOL &
& \H TAKAHASHI' &
& PAT-73-054006 JAPAN &
& \JULY 30, 1973' >
- 0000493 * SYNTHESIS REACTOR WITH PARTICULAR COOLING MEANS FOR EXOTHERMIC
REACTIONS AT HIGH PRESSURE &
& \G PAGANI, G GRAMATICA' &
& PAT-03753662 \USA' &
& \AUGUST 21, 1973' &
& AMMONIA METHANOL >

- 0000494 * METHANOL PRODUCTION &
 & \AJ CONNELL, A PINTO' &
 & PAT-03940428 \USA' &
 & \FEBRUARY 24, 1976' &
 & RECYCLE >
- 0000495 * PROCESS FOR EXOTHERMIC REACTIONS &
 & \W FUCHS' &
 & PAT-03941969 \USA' &
 & \MARCH 2, 1976' &
 & METHANOL AMMONIA-SYNTHESIS >
- 0000496 * SYNTHESIS PLANT &
 & \F CIECHOWSKI' &
 & PAT-03957449 \USA' &
 & \MAY 18, 1976' &
 & METHANOL AMMONIA LARGE-SCALE >
- 0000497 * OPTIMIZATION OF THE YIELD OF A CHEMICAL REACTION &
 & \JL MELENNEC' &
 & PAT-02220533 FRANCE &
 & \DECEMBER 6, 1974' >
- 0000498 * COMPUTER CONTROL AND OPTIMIZATION OF A LARGE METHANOL PLANT &
 & \MJ SHAH, RE STILLMAN' &
 & \IND ENG CHEM, V62, NO 12, DEC 1970, P59-75' >
- 0000499 * PRODUCTION OF GAS MIXTURES FOR METHANOL &
 & \FW DEJAHN' &
 & PAT-02393715 \USA' &
 & \AUGUST 28, 1945' &
 & PROPANE STEAM-REFORMING >
- 0000500 * METHANOL PRODUCTION FROM A HYDROCARBON FEEDSTOCK &
 & \AJ CONNELL, A PINTO' &
 & \BRIT 6 P.' &
 & PAT-01262479 U.K. &
 & \FEBRUARY 2, 1972' &
 & SYNTHESIS-GAS CARBON-DIOXIDE REMOVAL >
- 0000501 * METHANOL PROCESS WITH RECYCLE &
 & \RV GREEN' &
 & PAT-03763205 \USA' &
 & \OCTOBER 2, 1973' &
 & GAS STEAM NATURAL-GAS >
- 0000502 * PROCESS FOR PRODUCING METHANOL &
 & \H HILLER, G HOCHGESAND, ET AL' &
 & PAT-03962300 \USA' &
 & \JUNE 8, 1976' &
 & HEAVY-OIL-STEAM-REFORMING-SHIFT >
- 0000503 * METHANOL SYNTHESIS &
 & \MO TARHAN' &
 & PAT-03689575 \USA' &
 & \SEPTEMBER 5, 1972' >
- 0000504 * METHANOL PRODUCTION &

- & \RL ESPINO, TS PLETZKE' &
 - & \U.S. 4 P.' &
 - & PAT-03888896 &
 - & \JUNE 10, 1975' &
 - & CATALYST LIQUID-PHASE >
- 0000505 * CATALYST HOMOGENEOUS PROCESS DEVELOPMENT, UNIVERSITY OF TEXAS,
CO CONVERSION CATALYST &
& \CHEM ENG NEWS, 4-26-76, P29' >
- 0000506 * HOMOGENEOUS CATALYST UNDER DEVELOPMENT &
& \CHEM ENG NEWS, APRIL 26, 1976, P29' >
- 0000507 * DEVELOPMENT OF CATALYSTS FOR HYDROGENATION OF CO. REVIEW &
& \CR LAHIRI, S RAY' &
& \CHEM AGE INDIA 1975, 26, 11, 843-8 ENG' >
- 0000508 * CATALYST &
& \AT LARSON' &
& PAT-01489497 \USA' &
& \APRIL 8, 1924' &
& METHANOL PRODUCTION >
- 0000509 * PRODUCTION OF OXYGENATED ORGANIC COMPOUNDS &
& \A MITTASCH, M PIER, ET AL' &
& PAT-01558559 \USA' &
& \OCTOBER 27, 1925' &
& METHANOL-FROM-CO ZINC CHROMIUM-OXIDE CATALYSTS >
- 0000510 * CATALYST FOR SYNTHETIC METHANOL PRODUCTION &
& \JC WOODRUFF, G BLOOMFIELD' &
& PAT-01608643 \USA' &
& \NOVEMBER 30, 1926' &
& ZINC IRON-OXIDES >
- 0000511 * CATALYST FOR SYNTHETIC METHANOL PRODUCTION &
& \JC WOODRUFF, G BLOOMFIELD' &
& PAT-01609593 \USA' &
& \DECEMBER 7, 1926' &
& IRON MAGNESIUM-OXIDES >
- 0000512 * CATALYST FOR SYNTHETIC-METHANOL PRODUCTION &
& \JC WOODRUFF, G BLOOMFIELD' &
& PAT-01625924 \USA' &
& \APRIL 26, 1927' >
- 0000513 * CATALYST FOR METHANOL MANUFACTURE AND METHOD OF PRODUCING SAME &
& \BF DODGE' &
& PAT-01908696 \USA' &
& \MAY 16, 1933' &
& METHANOL-SYNTHESIS ZINC COPPER-OXIDE >
- 0000514 * CATALYST FOR SYNTHETIC METHANOL PRODUCTION &
& \JC WOODRUFF, G BLOOMFIELD' &
& PAT-01625925 \USA' &
& \APRIL 26, 1927' &
& ZINC-OXIDE >

- 0000515 * CATALYST FOR SYNTHETIC METHANOL PRODUCTION &
 & \JC WOODRUFF, G BLOOMFIELD' &
 & PAT-01625926 \USA' &
 & \APRIL 26, 1927' &
 & METAL-OXIDE CHLORIDE >
- 0000516 * CATALYST FOR SYNTHETIC METHANOL PRODUCTION &
 & \JC WOODRUFF, G BLOOMFIELD' &
 & PAT-01625927 \USA' &
 & \APRIL 26, 1927' &
 & METAL-OXIDE HALIDE >
- 0000517 * CATALYST FOR SYNTHETIC METHANOL PRODUCTION &
 & \JC WOODRUFF, G BLOOMFIELD' &
 & PAT-01625928 \USA' &
 & \APRIL 26, 1927' &
 & ZINC COPPER-OXIDES >
- 0000518 * CATALYST FOR SYNTHETIC METHANOL PRODUCTION &
 & \JC WOODRUFF, G BLOOMFIELD' &
 & PAT-01625929 \USA' &
 & \APRIL 26, 1927' &
 & ZINC CHROMIUM IRON-OXIDES >
- 0000519 * SYNTHESIS OF ORGANIC COMPOUNDS &
 & \HH STORCH' &
 & PAT-01681750 \USA' &
 & \AUGUST 21, 1928' &
 & METHANOL PRODUCTION COPPER-BASED-CATALYST >
- 0000520 * SYNTHESIS OF METHANOL &
 & \HH STORCH' &
 & PAT-01681751 \USA' &
 & \AUGUST 21, 1928' &
 & PRODUCTION CATALYSTS COPPER-METAL-FLUORIDES >
- 0000521 * SYNTHESIS OF METHANOL &
 & \HH STORCH' &
 & PAT-01681753 \USA' &
 & \AUGUST 21, 1928' &
 & PRODUCTION CATALYSTS METAL-OXIDE PALLADIUM >
- 0000522 * CATALYST FOR SYNTHETIC METHANOL PRODUCTION &
 & \JC WOODRUFF, G BLOOMFIELD, ET AL' &
 & PAT-01695447 \USA' &
 & \DECEMBER 18, 1928' &
 & NICKEL >
- 0000523 * PROCESS AND CATALYST FOR THE SYNTHESIS OF METHANOL &
 & \HH STORCH' &
 & PAT-01707331 \USA' &
 & \APRIL 2, 1929' &
 & PRODUCTION COPPER CERIUM-FLUORIDE >
- 0000524 * PROCESS AND CATALYST FOR SYNTHESIS OF METHANOL &
 & \HH STORCH' &
 & PAT-01738971 \USA' &
 & \DECEMBER 13, 1929' &

& PRODUCTION COPPER-OXIDE MAGNESIUM-OXIDE SILICA >

- 0000525 * MANUFACTURE OF METHYL ALCOHOL &
& \M DREYFUS' &
& PAT-01738989 \USA' &
& \DECEMBER 10, 1929' &
& METHANOL PRODUCTION CATALYST ZINC-OXIDE >
- 0000526 * PROCESS OF REDUCING PRODUCTS OF CO &
& \AO JAEGER' &
& PAT-01741307 \USA' &
& \DECEMBER 31, 1929' &
& METHANOL PRODUCTION CATALYST-CONCENTRATIONS 3 STAGE-REACTION >
- 0000527 * PROCESS OF REDUCING PRODUCTS OF CO &
& \AO JAEGER' &
& PAT-01741308 \USA' &
& \DECEMBER 31, 1929' &
& METHANOL PRODUCTION CATALYSTS OXIDATION
REDUCTION-CATALYST-COMBINATIONS >
- 0000528 * CATALYST AND CATALYTIC PROCESS &
& \WA LAZIER' &
& PAT-01746781 \USA' &
& \FEBRUARY 11, 1930' &
& METHANOL PRODUCTION METAL-OXALATES >
- 0000529 * CATALYTIC PROCESS &
& \WA LAZIER' &
& PAT-01746783 \USA' &
& \FEBRUARY 11, 1930' &
& METHANOL PRODUCTION ZINC MAGNESIUM-CHROMITES >
- 0000530 * PROCESS FOR THE MANUFACTURE OF ZINC-OXIDE CATALYSTS &
& \W BADER, SJ GREEN' &
& PAT-01793350 \USA' &
& \FEBRUARY 17, 1931' &
& METHANOL PRODUCTION >
- 0000531 * PROCESS FOR THE MANUFACTURE OF METHANOL &
& \G NATTA' &
& PAT-01815677 \USA' &
& \JULY 21, 1931' &
& PRODUCTION CATALYSTS SMITHSONITE ZINC-CARBONATE >
- 0000532 * PROCESS OF TRANSFORMING OXIDES OF CARBON INTO ORGANIC COMPOUNDS,
PARTICULARLY METHANOL &
& \O SCHMIDT, J UFER' &
& PAT-01818165 \USA' &
& \AUGUST 11, 1931' &
& PRODUCTION CATALYSTS COPPER ZINC-OXIDES >
- 0000533 * MANUFACTURE OF METHYL ALCOHOL AND OTHER OXYGENATED ORGANIC
COMPOUNDS &
& \M PIER' &
& PAT-01823468 \USA' &
& \SEPTEMBER 15, 1931' &
& PRODUCTION STAINLESS-STEEL-REACTORS >

- 0000534 * PROCESS OF PRODUCING REDUCTION PRODUCTS OF CO &
 & \AO JAEGER' &
 & PAT-01824896 \USA' &
 & \SEPTEMBER 29, 1931' &
 & METHANOL CATALYSTS MIXED-OXIDATION REDUCTION-CATALYSTS
 2 STAGE-REACTOR >
- 0000535 * PROCESS OF PRODUCING REDUCTION PRODUCTS OF CARBON-DIOXIDE &
 & \AO JAEGER' &
 & PAT-01831179 \USA' &
 & \NOVEMBER 10, 1931' &
 & METHANOL OXIDATION CATALYSTS >
- 0000536 * ZEOLITE PRODUCT &
 & \AO JAEGER, JA BERTSCH' &
 & PAT-01840450 \USA' &
 & \JANUARY 12, 1932' &
 & CATALYSTS METHANOL PRODUCTION >
- 0000537 * PRODUCING OXYGENATED ORGANIC COMPOUNDS &
 & \M PIER, R WIETZEL, ET AL' &
 & PAT-01841910 \USA' &
 & \JANUARY 19, 1932' &
 & METHANOL ZINC IRON CHROMIUM-OXIDE CATALYSTS >
- 0000538 * MANUFACTURE OF METHYL ALCOHOL &
 & \H DREYFUS' &
 & PAT-01868096 \USA' &
 & \JULY 19, 1932' &
 & METHANOL-SYNTHESIS COPPER ZINC-OXIDE CATALYST >
- 0000539 * PROCESS AND CATALYST FOR THE SYNTHESIS OF METHANOL &
 & \HH STORCH' &
 & PAT-01875273 \USA' &
 & \AUGUST 30, 1932' &
 & COPPER CALCIUM-OXIDE >
- 0000540 * PRODUCING OXYGENATED ORGANIC COMPOUNDS &
 & \M PIER, R WIETZEL, ET AL' &
 & PAT-01917323 \USA' &
 & \JULY 11, 1933' &
 & METHANOL-SYNTHESIS-CATALYSTS IRON COBALT-OXIDES >
- 0000541 * METHANOL MANUFACTURE AND CATALYST THEREFOR &
 & \BF DODGE' &
 & PAT-02014883 \USA' &
 & \SEPTEMBER 17, 1935' &
 & METHANOL-SYNTHESIS ZINC COPPER-OXIDE >
- 0000542 * PRODUCTION OF METHANOL AND OTHER CARBON COMPOUNDS AND
 CATALYTIC AGENTS FOR USE THEREIN &
 & \AT LARSON' &
 & PAT-02061470 \USA' &
 & \NOVEMBER 17, 1936' &
 & METHANOL-SYNTHESIS COPPER MANGANESE-OXIDE >
- 0000543 * PROCESS OF OBTAINING METHANOL &

- & \WD WILCOX' &
 - & PAT-02279153 \USA' &
 - & \APRIL 7, 1942' &
 - & METHANOL-SYNTHESIS ZINC-OXIDE COPPER-CATALYSTS >
- 0000544 * CATALYSTS FOR HYDROCARBON SYNTHESIS &
 - & \EE SENSEL, RA BECK' &
 - & PAT-02517035 \USA' &
 - & \AUGUST 1, 1950' &
 - & LANTHANUM-OXIDE METHANOL-SYNTHESIS >
- 0000545 * SUPPORTED CATALYSTS FOR THE CONVERSION OF CO CONTAINING
 REACTANTS &
 - & \EE SENSEL, MM STEWART' &
 - & PAT-02517036 \USA' &
 - & \AUGUST 1, 1950' &
 - & SILICA ALUMINA METAL-OXIDE-CATALYST METHANOL-SYNTHESIS >
- 0000546 * PROCESS FOR PREPARING A CU-ZN-CR SYSTEM CATALYST COMPOSITION &
 - & \T EGUCHI, T YAMAMOTO, ET AL' &
 - & PAT-03256208 \USA' &
 - & \JUNE 14, 1966' &
 - & CUPRAMMONIUM ZINC-CHROMATE METHANOL-SYNTHESIS CATALYST >
- 0000547 * PRODUCTION OF OXYGENATED HYDROCARBONS &
 - & \P DAVIES, FF SNOWDON' &
 - & PAT-03326956 \USA' &
 - & \JUNE 20, 1967' &
 - & METHANOL-SYNTHESIS COPPER ZINC CHROMIUM-OXIDE CATALYST >
- 0000548 * PROCESS FOR THE CATALYTIC SYNTHESIS OF METHANOL &
 - & \T EGUCHI, T YAMAMOTO, ET AL' &
 - & PAT-03376332 \USA' &
 - & \APRIL 2, 1968' &
 - & METHANOL-SYNTHESIS CATALYST CUPRAMMONIUM-CHROMATE >
- 0000549 * CATALYST FOR THE MANUFACTURE OF METHANOL &
 - & \SM COLLINS' &
 - & PAT-02302658 GERMANY &
 - & \AUGUST 2, 1973' >
- 0000550 * OXIDE CATALYSTS FOR PREPARATION OF METHANOL FROM CARBON OXIDES
 AND HYDROGEN &
 - & \S ASANO, T NAKAMURA' &
 - & \GER OFFEN 11 P.' &
 - & PAT-02365001 GERMANY &
 - & \JULY 10, 1975' &
 - & HYDROGENATION >
- 0000551 * METHANOL &
 - & \NS IMYANITOV, BE KEVAEV, ET AL' &
 - & PAT-00374270 USSR &
 - & \MARCH 20, 1973' >
- 0000552 * PRODUCTION OF METHANOL &
 - & \EF MAGOON' &
 - & PAT-03709919 \USA' &
 - & \JANUARY 9, 1973' >

- 0000553 * COPPER, ZINC, DIDYMIUM OXIDE-CONTAINING CATALYSTS &
& \EF MAGOON, LH SLAUGH' &
& PAT-03758417 \USA' &
& \SEPTEMBER 11, 1973' >
- 0000554 * METHOD OF MAKING A METHANOL SYNTHESIS CATALYST &
& \M COLLINS' &
& PAT-03850850 \USA' &
& \NOVEMBER 26, 1974' &
& SPINEL COPPER-OXIDE >
- 0000555 * ALUMINUM COPPER ZINC BORON OXIDE CATALYST FOR PREPARING
METHANOL FROM CO AND HYDROGEN &
& \T NAKAMURA, S ASANO, ET AL' &
& PAT-02449493 GERMANY &
& \APRIL 30, 1975' >
- 0000556 * METHANOL SYNTHESIS CATALYST &
& \D CORNTHWAITE' &
& PAT-03923694 \USA' &
& \DECEMBER 2, 1975' >
- 0000557 * PROCESS FOR METHANOL SYNTHESIS &
& \S ASANO, T NAKAMURA' &
& PAT-03939191 \USA' &
& \FEBRUARY 17, 1976' &
& CATALYST OXIDES COPPER ZINC BORON >
- 0000558 * PRODUCTION OF OXYGENATED ORGANIC COMPOUNDS &
& \W BADER, EB THOMAS' &
& PAT-01942530 \USA' &
& \JANUARY 9, 1934' &
& METHANOL-SYNTHESIS-CATALYST ZINC-SULFIDE >
- 0000559 * PROCESS FOR PRODUCING METHANOL &
& \R HERBERT, H LIEBIGT' &
& PAT-03897471 \USA' &
& \JULY 29, 1975' &
& COPPER VANADIUM ZINC MANGANESE-OXIDE-CATALYST >
- 0000560 * SYNTHESIS OF METHANOL AT LOW PRESSURES &
& \IV DOMBALOV, D SHISHKOV' &
& \ZH PRIKL KHM, LENINGRAD 1973, 46, 3, 628-31 RUSS' >
- 0000561 * QUALITY OF CRUDE METHANOL FROM LOW-TEMPERATURE SYNTHESIS AT 50 ATM
& \VV LENDER, EN TSYBINA, ET AL' &
& \KHM PROM, MOSCOW, 1973, 49, 12, 899-901 RUSS' >
- 0000562 * DETERMINATION OF THE FORMATION RATE OF METHANOL ON A
LOW-TEMPERATURE CATALYST &
& \VV LENDER, LS PARFENOVA, ET AL' &
& \KHM PROM, MOSCOW, 1973, 49, 9, 654-5 RUSS' >
- 0000563 * EFFECT OF THE RUNNING TIME ON THE ACTIVITY OF A LOW-TEMPERATURE
CATALYST FOR METHANOL SYNTHESIS &
& \IG POPOV, YV LENDER, ET AL' &
& \KHM PROM-ST, MOSCOW 1975, 5, 339-40 RUSS' >

- 0300564 * EFFECT OF GAS COMPOSITION ON THE PRODUCTIVITY OF METHANOL UNITS &
& \AP SELITSKII' &
& \KHIM PROM-ST, MOSCOW 1975, 5, 397 RUSS' >
- 0300565 * USE OF OXYGEN-CONTAINING GASES FOR THE SYNTHESIS OF METHANOL
ON A ZINC-CHROMIUM CATALYST &
& \NA GAVRYA, VI ATROSHCHENKO, ET AL' &
& \KHIM TEKHNOL, KIEV 1975, 2, 8-10 RUSS' >
- 0300566 * ADSORPTION AND DESORPTION OF HYDROGEN, CO, AND
THEIR REACTION PRODUCTS ON A CATALYST FOR THE SYNTHESIS OF
METHANOL &
& \C AHARONI, H STARER' &
& \CAN J CHEM 52 24 4044-9' &
& \1974' &
& ZINC COPPER >
- 0300567 * ROLE OF ZINC CHROMITE IN ZINC-CHROMIUM CATALYSTS FOR
METHANOL SYNTHESIS &
& \VL CHERNOBRIVETS, MT RUSOV' &
& \KATAL KATAL 1974, 12, 60-5 RUSS' >
- 0300568 * MECHANISM OF METHANOL SYNTHESIS FROM CO AND HYDROGEN STUDIES
USING THE CARBON-14 ISOTOPE &
& \YS KAGAN, AY ROZOVSKII, ET AL' &
& \DOKL AKAD NAUK SSSR 1975, 224, 5, 1081-4 CHEM, RUSS' >
- 0300569 * TECHNICAL REACTIONS OF CO WITH METAL CARBONYLS AS CATALYSTS &
& \J FALBE' &
& \J ORGANOMET CHEM 1975, 94, 2, 213-27 GER' >
- 0300570 * SYNTHESIS OF ALCOHOLS ACCORDING TO THE REPPE REACTION &
& \MM BOGORADOVSKAYA, NS IMYANITOV, ET AL' &
& \ZH PRIKL KHIM, LENINGRAD 1973, 46, 3, 616-19 RUSS' >
- 0300571 * CARBONYLATION REACTIONS. 10 - CARBONYLATION OF ETHYLENE BY CO
IN METHANOL IN THE PRESENCE OF COPPER \II' CHLORIDE &
& \BK NEFEDOV, NS SERGEEVA, ET AL' &
& \IZV AKAD NAUK SSSR, SER KHIM 1973, 4, 808-10' >
- 0300572 * OXO PROCESS &
& \FJ DEFFNER' &
& PAT-03733361 \USA' &
& \MAY 15, 1973' >
- 0300573 * PROCESS FOR PRODUCING ALCOHOLS &
& \CE CARTER, BH GWYNN' &
& PAT-02759025 \USA' &
& \AUGUST 14, 1956' &
& ALKENES >
- 0300574 * OXO-SYNTHESIS GAS &
& \B REYNOLDS' &
& PAT-03919113 \USA' &
& \NOVEMBER 11, 1975' >
- 0300575 * PRODUCTION OF OXYGENATED CARBON COMPOUNDS &

- & NO ROELEN' &
 & PAT-02327066 \USA' &
 & \AUGUST 17, 1943' &
 & CARBONYLATION ALKENES ALDEHYDES KETONES ALCOHOLS >
- 0000576 * CATALYTIC REDUCTION OF CARBONYL COMPOUNDS &
 & \AO JAEGER' &
 & PAT-01834621 \USA' &
 & \DECEMBER 1, 1931' &
 & ZEOLITE-CATALYSTS >
- 0000577 * REACTION OF CO WITH HYDROGEN TO FORM ALCOHOLS &
 & \W HIMMLER, G SCHILLER' &
 & PAT-02787628 \USA' &
 & \APRIL 2, 1957' >
- 0000578 * SYNTHESIS OF HIGHER ALIPHATIC ALCOHOLS FROM CO AND HYDROGEN &
 & \VYSSH ZHIRNYE SPIRITY, 11, 238-250' >
- 0000579 * CARBONYLATION REACTIONS. 8. CARBONYLATION OF 1 PROPANOL AND
 1 BUTANOL BY CO IN THE PRESENCE OF COPPER(II) CHLORIDE &
 & \BK NEFEDOV, NS SERGEEVA, ET AL' &
 & \IZV AKAD NAUK SSSR, SER KHIM 1973, 4, 804-6 RUSS' >
- 0000580 * SYNTHESIZING HIGHER MOLECULAR ORGANIC COMPOUNDS CONTAINING
 OXYGEN &
 & \G WIETZEL, R WIETZEL' &
 & PAT-01562480 \USA' &
 & \NOVEMBER 24, 1925' &
 & ACID ALDEHYDE ESTER ALCOHOL METHANOL ETHANOL >
- 0000581 * ISOLATION OF C5-C18 AND C1-C4 ALIPHATIC ALCOHOLS FROM
 HYDROGENATED PRODUCTS OF HIGHER FATTY ALCOHOL SYNTHESIS FROM
 CO AND HYDROGEN &
 & \VS TIMOFEEV, TG PAVLENKO, ET AL' &
 & PAT-00480694 USSR &
 & \AUGUST 15, 1975' >
- 0000582 * THERMOMAGNETIC ANALYSIS OF MOLTEN IRON CATALYSTS FOR THE
 SYNTHESIS OF HIGHER ALCOHOLS FROM CO AND HYDROGEN &
 & \SM LOKTEV, LI MAKARENKOVA, ET AL' &
 & \KINET KATAL 1972, 13, 4, 1042-9 RUSS' >
- 0000583 * FORMATION AND STRUCTURAL FEATURES OF THE GRAINS OF AN IRON
 CATALYST FOR THE SYNTHESIS OF HIGHER ALCOHOLS FROM CO AND
 HYDROGEN &
 & \SM LOKTEV, AN BASHKIROV, ET AL' &
 & \KINET KATAL 1973, 14, 1, 217-23 RUSS' >
- 0000584 * DISTRIBUTION OF ALCOHOLS AND ACIDS ON FRACTIONATION OF SYNTHESIS
 PRODUCTS FROM CO AND WATER VAPOR &
 & \SI SMOLYANINOV, AV KRAVTSOV, ET AL' &
 & \SB TR MOLODYKH UCH TOMSK POLITEKH INST NO 1 130-2' &
 & \1973' >
- 0000585 * REACTION OF ORGANOBORANES CONTAINING A TERTIARY ALKYL GROUP
 WITH CO. NEW APPROACH TO THE SYNTHESIS OF HIGHLY
 BRANCHED TRIALKYLCARBINOLS &

& NE NEGISHI, MC BROWN' &
 & \SYNTHESIS 4 197-9' &
 & \1972' &
 & PREPARATION CARBONYLATION >

- 0000586 * CATALYTIC MANUFACTURE OF POLYFUNCTIONAL, OXYGEN-CONTAINING
 PRODUCTS OR THEIR DERIVATIVES &
 & \RL PRUETT, WE WALKER' &
 & \GER OFFEN 43 P.' &
 & PAT-02262319 \USA' &
 & \JUNE 28, 1973' &
 & PROPYLENE ETHYLENE-GLYCOL GLYCEROL >
- 0000587 * CATALYTIC HYDROGENATION OF CO &
 & \WE WALKER, ES BROWN, JR' &
 & PAT-02531113 GERMANY &
 & \JANUARY 29, 1976' >
- 0000588 * CATALYTIC PROCESS FOR POLYHYDRIC ALCOHOLS AND DERIVATIVES &
 & \JN CAUSE' &
 & PAT-03948965 \USA' &
 & \APRIL 6, 1976' &
 & BIS(TRIORGANO PHOSPHINE)IMINIUM-CATION
 RHODIUM-CARBONYL-COMPLEX >
- 0000589 * CATALYTIC PROCESS FOR POLYHYDRIC ALCOHOLS AND DERIVATIVES &
 & \WE WALKER, JR BRYANT, ET AL' &
 & PAT-03952039 \USA' &
 & \APRIL 20, 1976' &
 & ETHER ESTER ALKALI-METAL-CATION RHODIUM-CARBONYL-COMPLEX >
- 0000590 * CATALYTIC PROCESS FOR POLYHYDRIC ALCOHOLS AND DERIVATIVES &
 & \RL PRUETT, WE WALKER' &
 & PAT-03957857 \USA' &
 & \MAY 18, 1976' &
 & RHODIUM-CARBONYL >
- 0000591 * CATALYTIC PRODUCTION OF ACIPIC ACID &
 & \BRIT 7 P. DIVISION OF BRIT 1,278,353' &
 & PAT-01278354 U.K. &
 & \JUNE 21, 1972' &
 & CARBONYLATION >
- 0000592 * 2 BUTYNE 1,4 DIOL FROM ACETYLENE AND FORMALDEHYDE &
 & \K SCHOENEMANN' &
 & PAT-02206693 GERMANY &
 & \AUGUST 16, 1973' >
- 0000593 * REACTION SPECIFICITY OF CO AND ITS APPLICATIONS TO SYNTHETIC
 CHEMISTRY &
 & \T SAEGUSA, T TSUDA' &
 & \KAGAKU, KYOTO, ZOKAN 1974, 63, 53-73 JAPAN' >
- 0000594 * SYNTHESIS OF ALDEHYDES &
 & \JD MCCLUFE' &
 & \U.S. 4 P.' &
 & PAT-03875240 &
 & \APRIL 1, 1975' &

& ALDEHYDE PREPARATION ETHYLENE >

- 0000595 * CATALYTIC PREPARATION OF ALDEHYDES FROM OLEFINS &
& \RA SCHNELL' &
& \U.S. 3 P.' &
& PAT-03752859 &
& \AUGUST 14, 1973' >
- 0000596 * CATALYTIC PREPARATION OF ALDEHYDES FROM OLEFINS, CO, AND ALCOHOLS &
& \LJ KEHOE' &
& PAT-03534103 \USA' &
& \OCTOBER 13, 1970' >
- 0000597 * 3,7 DIMETHYL 1 OCTANAL &
& \M TANOMURA, T NISHIDA, ET AL' &
& PAT-73-039415 JAPAN &
& \JUNE 9, 1973' >
- 0000598 * HEXAMETHYLTRIS-O-HOMOTROPONE FROM 3,3 DIMETHYLCYCLOPROPENE
AND CO &
& \P BINGER, U SCHUCHARDT' &
& \ANGEW CHEM 1975, 87, 19, 715 GER' >
- 0000599 * OPTICALLY ACTIVE ALPHA-PHENYLPROPIONALDEHYDE &
& PAT-73-099131 JAPAN &
& \DECEMBER 15, 1973' >
- 0000600 * SYNTHESIS OF DIETHYL KETONE FROM ETHYLENE AND CO &
& \MV KHOKHLOVA, NS IMYANITOV' &
& \NEFTEPERERAB NEFTEKHIM, MOSCOW 1976, 1, 25-6 RUSS' >
- 0000601 * PREPARATION OF DIETHYL KETONE FROM ETHYLENE AND CO.
REVIEW &
& \NS IMYANITOV, OM RUOKOVSKII, ET AL' &
& \GIDROFORMILIROVANIE 161-70' &
& \1972' >
- 0000602 * REACTION OF ALKYL COPPER \I' COMPLEXES WITH CO.
NEW KETONE SYNTHESIS &
& \J SCHWARTZ' &
& \TETRAHEDRON LETT 28 2803-6' &
& \1972' &
& PREPARATION CARBONYLATION >
- 0000603 * A CONVENIENT HIGH YIELD DICOBALT OCTACARBONYL CATALYZED
SYNTHESIS OF DIARYL KETONES FROM DIARYLMERCURY COMPOUNDS AND CO &
& \J SEYFERTH, RJ SPOHN' &
& \J AM CHEM SOC, 91, 22, OCT 22, 1969, P5192-93' >
- 0000604 * REACTIONS OF CO WITH ORTHO-METHYL AND ORTHO-HYDROXYMETHYLPHENOLS &
& \HE HOLMQUIST' &
& \J ORG CHEM V34, NO 12, DEC 1969, P4164-65' >
- 0000605 * ACRYLIC ACID OR ACRYLATES &
& \S SHODA, Y SUZUKI, ET AL' &
& PAT-74-027166 JAPAN &
& \JULY 16, 1974' >

- 0000606 * CATALYTIC PRODUCTION OF OXYGENATED ORGANIC COMPOUNDS &
 & \DG KUPER, WB HUGHES' &
 & \U.S. 3 P.' &
 & PAT-03746747 &
 & \JULY 17, 1973' &
 & OLEFIN CARBOXYLATION ESTER PREPARATION >
- 0000607 * CATALYTIC PREPARATION OF CARBOXYLIC-ACID ESTERS FROM OLEFINS,
 ALCOHOLS, AND CO IN THE PRESENCE OF A KETONE
 PROMOTER &
 & \RA SCHELL' &
 & \U.S. 5 P.' &
 & PAT-03660439 &
 & \MAY 2, 1972' >
- 0000608 * CATALYTIC PREPARATION OF CARBOXYLIC-ACID ESTERS FROM OLEFINS,
 ALCOHOLS, AND CO IN THE PRESENCE OF AN ALKYL ETHER
 AND AN ACTIVATOR AMOUNT OF WATER &
 & \RA SCHELL' &
 & \U.S. 4 P.' &
 & PAT-03661948 &
 & \MAY 9, 1972' >
- 0000609 * CARBOXYLIC ACID ESTERS BY LOW-PRESSURE HYDROFORMYLATION OF OLEFINS
 IN BENZIL &
 & \K BOTT' &
 & \ANGEW CHEM 1973, 85, 20, 911-13 GER' >
- 0000610 * CATALYST FOR THE PREPARATION OF ALKYL ESTER OF FORMIC ACID &
 & \M ICHIKAWA, A UCHIDA' &
 & \JAPAN, KOKAI 3 P.' &
 & PAT-74-117387 JAPAN &
 & \NOVEMBER 9, 1974' &
 & ALCOHOL METHYL >
- 0000611 * CATALYTIC PRODUCTION OF CARBOXYLIC ESTERS &
 & \T KAJIMOTO, S WAKAMATSU, ET AL' &
 & PAT-03723486 \USA' &
 & \MARCH 27, 1973' >
- 0000612 * FATTY-ACID SYNTHESIZING PROCESS, ESTER PRODUCING SYNTHETIC
 FATTY-ACID PROCESS, JAPAN CHEMICAL INDUSTRY RESEARCH INSTITUTE &
 & \CHEM ECON ENG REV, 3-76, P45' >
- 0000613 * RECOVERY OF CATALYSTS IN ESTERIFICATION OF ALCOHOLS WITH
 OLEFINS AND CO &
 & \H ISA, T INAGAKI, ET AL' &
 & PAT-75-062888 JAPAN &
 & \MAY 29, 1975' >
- 0000614 * METHYL ACETATE FROM METHANOL AND CO &
 & \RG SCHULTZ' &
 & PAT-01939286 GERMANY &
 & \OCTOBER 29, 1970' >
- 0000615 * PROCESS FOR PRODUCING METHYL FORMATE &
 & \H WAKAMATSU, K SHIMOMURA' &
 & PAT-03816513 \USA' &

& \JUNE 11, 1974' &
& CARBONYLATION METHANOL >

- 0000616 * REACTIONS OF METHYL ALCOHOL WITH CO AND HYDROGEN IN THE
PRESENCE OF COBALT CARBONYLS &
& \G ALEANESI' &
& \CHIM IND, MILAN 1973, 55, 4, 319-22 ITAL' >
- 0000617 * METHYLENE DIACETATE &
& \SJ LAPORTE, WG TOLAND' &
& PAT-03927078 \USA' &
& \DECEMBER 16, 1975' >
- 0000618 * METHYLENE DIPROPIONATE &
& \SJ LAPORTE, WG TOLAND' &
& PAT-02302568 GERMANY &
& \AUGUST 2, 1973' >
- 0000619 * UNSATURATED CARBOXYLIC ACIDS AND THEIR DERIVATIVES &
& \H FUKUTANI, M TOKIZAWA, ET AL' &
& PAT-75-000645 JAPAN &
& \JANUARY 10, 1975' >
- 0000620 * POLYOL CARBOXYLATES &
& \H ISA, T INAGAKI, ET AL' &
& PAT-02404955 GERMANY &
& \AUGUST 29, 1974' >
- 0000621 * MALONIC ACID DIALKYL ESTERS &
& \M EL-CHAHAWI, U PRANGER, ET AL' &
& PAT-02359963 GERMANY &
& \JUNE 5, 1975' >
- 0000622 * CARBONYLATION OF SOME ALIPHATIC ETHERS WITH CO UNDER PRESSURE &
& \SK PALIT, MK SAXENA, ET AL' &
& \INDIAN J OF TECH, V7, OCT 1969, P329-332' >
- 0000623 * ETHYLENIC ACIDS AND THEIR DERIVATIVES &
& \GI MYAGKOVA, VP NECHIPORENKO, ET AL' &
& \DOKL VSES KONF KHIM ATSETILENA, 4TH 1972, 1, 233-5 RUSS' >
- 0000624 * CARBONYLATION OF ALIPHATIC ORGANIC HALIDES WITH METALLIC
ALCOHOLATES &
& \RN KNOWLES' &
& PAT-03772394 \USA' &
& \NOVEMBER 13, 1973' >
- 0000625 * ALKYL ARYLACETATES &
& \M EL-CHAHAWI, H RICHTZENHAIN' &
& PAT-02240398 GERMANY &
& \FEBRUARY 28, 1974' >
- 0000626 * ALKYL ARYLACETATES &
& \M EL-CHAHAWI, H RICHTZENHAIN' &
& PAT-02240399 GERMANY &
& \FEBRUARY 28, 1974' >
- 0000627 * 5 FORMYLVALERIC ACID ESTERS &

& \A MATSUDA' &
 & PAT-73-085530 JAPAN &
 & \NOVEMBER 13, 1973' >

- 0000628 * LACTONES FROM DIOLEFINS OR DIALCOHOLS &
 & \Y SOMA, H SANO' &
 & \JAPAN, KOKAI 3 P.' &
 & PAT-74-061166 JAPAN &
 & \JUNE 13, 1974' &
 & ALCOHOL PREPARATION >
- 0000629 * CARBONYLATION REACTIONS. 4 - INTERMEDIATE PRODUCTS FROM THE
 REACTION FORMING BETA ALKOXYPROPIONIC ACID ESTERS FROM ETHYLENE,
 CO, AND ALIPHATIC ALCOHOLS IN THE PRESENCE OF
 MERCURY ACETATE &
 & \BK NEFEDOV, NS SERGEEVA, ET AL' &
 & \IZV AKAD NAUK SSSR SER KHIM 11 2494-6' &
 & \1972' >
- 0000630 * CARBONYLATION OF OLEFINS AND ALCOHOLS WITH CO IN AN ANTIMONY\V'
 CHLORIDE-HYDROCHLORIC ACID-LIQUID SULFUR DIOXIDE MEDIUM &
 & \KV PUZITSKII, SD PIROZHKOV, ET AL' &
 & \IZV AKAD NAUK SSSR, SER KHIM 1974, 1, 202-3 RUSS' >
- 0000631 * FORMIC ACID PROCESS NEW, ALKYL FORMATE PRODUCING PROCESS NEW,
 ALCOHOL PRODUCING PROCESS NEW, BETHLEHEM STEEL CORP &
 & \FARM CHEM, 1-76, P115' >
- 0000632 * SYNTHESIS OF SODIUM FORMATE FROM WASTE GASES OF AMMONIA
 PRODUCTION &
 & \EY DORFMAN, AM KUNIN' &
 & \KHIM PROM, MOSCOW 1973, 49, 6, 425-6 RUSS' >
- 0000633 * CONTINUOUS PRODUCTION OF SODIUM FORMATE &
 & \I TAGUCHI, K OYA, ET AL' &
 & PAT-73-075509 JAPAN &
 & \OCTOBER 11, 1973' >
- 0000634 * SODIUM FORMATE &
 & \EY DORFMAN, AM KUNIN' &
 & PAT-00468909 USSR &
 & \APRIL 30, 1975' >
- 0000635 * ACETIC ACID, CO, DAIGEL LTD, HYDROGEN, METHANOL PROCESS,
 MONSANTO CO &
 & \JPN CHEM WEEK, 11-6-75, P2' >
- 0000636 * ACETIC ACID, CO &
 & \DUPONT, NATIONAL DISTILLERS AND CHEMICAL CORP' &
 & \EUR CHEM NEWS, 17-10-75, P36' >
- 0000637 * VAPOR PHASE CARBONYLATION OF METHANOL TO ACETIC-ACID &
 & \RG SCHULTZ, PD MONTGOMERY' &
 & \AMER CHEM SOC, DIV PETROL CHEM, PREPR 1972, 17, 1, 813-818 ENG' >
- 0000638 * CATALYST FOR PREPARATION OF ACETIC-ACID &
 & \M ICHIKAWA, A UDA, ET AL' &
 & \JAPAN, KOKAI 4 P.' &

- & PAT-73-041987 JAPAN &
& \JUNE 19, 1973' &
& METHANOL >
- 0000639 * ACETIC-ACID &
& \M MORITA, S SATO' &
& PAT-74-013109 JAPAN &
& \FEBRUARY 5, 1974' >
- 0000640 * ACETIC-ACID &
& \T ONOUCHI, S MATSUHIRA' &
& PAT-73-049712 JAPAN &
& \JULY 13, 1973' >
- 0000641 * ACETIC-ACID &
& \T ONOUCHI, S MATSUHIRA' &
& \JAPAN, KOKAI 5 P.' &
& PAT-73-049713 JAPAN &
& \JULY 13, 1973' &
& METHANOL CATALYST PREPARATION >
- 0000642 * ACETIC-ACID FROM METHANOL &
& \T ONOUCHI, S MATSUHIRA' &
& PAT-73-080511 JAPAN &
& \OCTOBER 29, 1973' >
- 0000643 * CATALYTIC PREPARATION OF CARBOXYLIC ACIDS &
& \OM FENTON' &
& \U.S. 2 P.' &
& PAT-3637833 &
& \JANUARY 25, 1972' &
& ETHYLENE >
- 0000644 * ALKANECARBOXYLIC ACIDS FROM ALKYL FORMATES AND CO &
& \N ISOGAI' &
& PAT-73-135053 JAPAN &
& \OCTOBER 25, 1973' >
- 0000645 * CONTINUOUS PREPARATION OF BRANCHED CARBOXYLIC-ACIDS VIA THE
REACTION OF CO WITH ALKENES &
& \T TROCSANYI, J LAKY' &
& \ROPA UHLIE 17 6 312-18' &
& \1975' &
& PROPYLENE >
- 0000646 * PURIFYING BRANCHED-CHAIN CARBOXYLIC-ACIDS PREPARED FROM OLEFINS
AND CO IN SULFURIC ACID &
& \Y KOMATSU, K FUJII, ET AL' &
& \JAPAN 6 P.' &
& PAT-73-035048 JAPAN &
& \OCTOBER 25, 1973' &
& PURIFICATION CARBOXYLATION >
- 0000647 * CARBONYLATION IN LIQUID SULFUR DIOXIDE. II - SELECTIVE FORMATION
OF SEVERAL CARBOXYLIC ACIDS BY CARBONYLATION IN THE ANTIMONYV
CHLORIDE-LIQUID SULFUR DIOXIDE SYSTEM &
& \M YOSHIMURA, M NOJIMA, ET AL' &
& \BULL CHEM SOC JAP 1973, 46, 7, 2164-5 ENG' >

- 0000648 * BRANCHED CARBOXYLIC ACIDS &
& \Y KOMATSU, T TAMURA, ET AL' &
& PAT-73-027413 JAPAN &
& \JULY 13, 1973' >
- 0000649 * TERTIARY CARBOXYLIC-ACIDS FROM C4 ALCOHOLS OR OLEFINS AND CO &
& \H SANO, Y SOMA' &
& \JAPAN, KOKAI 5 P.' &
& PAT-74-048616 JAPAN &
& \MAY 11, 1974' &
& PREPARATION >
- 0000650 * CARBONYLATION REACTIONS COMMUNICATION 10. CARBONYLATION OF
ETHYLENE OXIDE WITH CO IN METHANOL MEDIUM IN THE PRESENCE
OF CUPRIC CHLORIDE &
& \JK NEFEDOV, NS SERGEEVA, ET AL' >
- 0000651 * SYNTHESIS OF BRANCHED CARBOXYLIC ACIDS FROM ALPHA-OLEFINS AND CO
IN THE PRESENCE OF BORON FLUORIDE DIHYDRATE &
& \EV LEBEDEV, PP GUSHCHIN, ET AL' &
& \NEFTEPERERAB NEFTEKHIM, KIEV 1972, NO 8, 7-11 RUSS' >
- 0000652 * NEOCARBOXYLIC ACIDS &
& \SD PIROZHKOV, KV PUZITSKII, ET AL' &
& PAT-00514751 USSR &
& \FEBRUARY 28, 1976' >
- 0000653 * CARBOXYLIC ACIDS FROM OLEFINS OR ALCOHOLS AND CO &
& \Y MATSUSHIMA, T KOYANO, ET AL' &
& PAT-75-123613 JAPAN &
& \SEPTEMBER 29, 1975' >
- 0000654 * TERTIARY CARBOXYLIC ACIDS FROM OLEFINS AND CO BY CONTINUOUS
PROCESS &
& \Y SOMA, H SANO' &
& PAT-75-123614 JAPAN &
& \SEPTEMBER 29, 1975' >
- 0000655 * CUPROUS SALT CATALYZED FATTY ACID SYNTHESIS &
& \H SANO, Y SOMA' &
& PAT-73-026530 JAPAN &
& \JUNE 21, 1973' >
- 0000656 * PREPARATION OF MONOCARBOXYLIC ACIDS BY CONVERSION OF
BRANCHED-CHAIN MONOOLEFINS WITH CO AND WATER UNDER THE
INFLUENCE OF LIQUID HYDROGEN FLUORIDE &
& \A KWANTES, B STOUTHAMER' &
& PAT-01174209 U.K. &
& \DECEMBER 17, 1969' >
- 0000657 * THE CARBONYLATION OF ALKYL HALIDE WITH CO IN THE SbCl5-LIQUID
SULFUR DIOXIDE SYSTEM &
& \M NOJIMA, K TATSUMI, ET AL' &
& \JULY 1971' >
- 0000658 * SYNTHESIS OF TERT-CARBOXYLIC ACIDS FROM OLEFINS AND CO BY
COPPER \I' CARBONYL CATALYST &

- & \Y SOUMA, H SANO, J IYODA' &
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& \1973' &
& PREPARATION >
- 0000660 * DICARBOXYLIC ACIDS &
& \Y SOMA, H SANO' &
& PAT-75-019713 JAPAN &
& \MARCH 1, 1975' >
- 0000661 * SUBSTITUTED AND UNSUBSTITUTED MALEIC ANHYDRIDES AND THE
CORRESPONDING ACETYLENIC ACIDS &
& \YA KUSHNIKOV, DV SOKOLSKII, ET AL' &
& PAT-00397506 USSR &
& \SEPTEMBER 17, 1973' >
- 0000662 * GLYCOLIC ACID AND OXYDIACETIC ACID &
& \S SUZUKI' &
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& \OCTOBER 7, 1975' >
- 0000663 * KINETIC STUDY ON THE SYNTHESIS OF METHYL GLYCOLATE FROM
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- 0000664 * ALPHA-ACYLOXYACETIC ACID &
& \VP KURKOV, SJ LAPPORTE, ET AL' &
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- 0000666 * NEWS-ITEM A CITRIC ACID SYNTHESIS FROM CO DERIVATIVES &
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& \MAY 7, 1975' >
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& \T ONOUCHI, S MATSUBIRA, ET AL' &
& PAT-75-047921 JAPAN &
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- 0000669 * ACETIC ANHYDRIDE &
& \T ONOUCHI, S MATSUBIRA, ET AL' &
& PAT-75-047922 JAPAN &
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 & \T KAGAWA, T KONO, ET AL' &
 & PAT-75-030823 JAPAN &
 & \MARCH 27, 1975' >

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 & \D FREUDENBERGER' &
 & PAT-02339633 GERMANY &
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0000672 * BETA, BETA-PRIME - DICHLOROISOBUTYRYL CHLORIDE &
 & \Y ODA, Y ARAI' &
 & PAT-73-054023 JAPAN &
 & \JULY 30, 1973' >

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 & \H ISA, T INAGAKI, ET AL' &
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0000674 * CARBOXYLIC ACID AMIDES &
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 & \OJ QUARTULLI, RJ KANDALL' &
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 & \L FRIEND, M VONSTEIN' &
 & PAT-03002816 \USA' &
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& PAT-01908484 \USA' &
& \MAY 9, 1933' &
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- 0000684 * PROCESS FOR PURIFYING GASES AND SYNTHESIS OF AMMONIA THEREFROM &
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& \U.S. 5 P.' &
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& AMMONIA CATALYST PREPARATION >
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& \I MAEDA, H KOIKE' &
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& PREPARATION BENZENE >
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II - DIRECT SYNTHESIS OF SCHIFF BASES FROM AROMATIC NITRO
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 & \N KONAMI, Y FUKUOKA, ET AL' &
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 & \J CHEM SOC, CHEM COMMUN 1973, 22, 853 ENG' >
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 & \KHIM GETEROTSIKL SOEDIN 7 10 1368' &
 & \1971' &
 & PREPARATION >
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& \SK NEFEDOV, NS SERGEEVA, ET AL' &
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- 0000701 * SYNTHESIS OF CALCIUM CYANAMIDE DURING THE ACTION OF AMMONIA AND
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& \SA YAKUBOV, SA SIGOV' &
& \UZB KHIM ZH 15 4 7-8' &
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& PREPARATION >
- 0000702 * INTEGRATED METHOD FOR PRODUCING UREA AND AMMONIA &
& \A BONETTI' &
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& \DECEMBER 18, 1975' >
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& \K MAYER' &
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& \MAY 21, 1970' >
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& \VI KUCHERYAVYI, OM GORLOVSKII, ET AL' &
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& \N IIDA' &
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CARBONYL SULFIDE, CO, AND WATER &
& \JJ HARPER' &
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& \V MACHO, J HUDEC, ET AL' &
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& \HA DIECK, RM LAINE, ET AL' &
& \J ORG CHEM 1975, 40, 19, 2819-22 ENG' >
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& \J CHEM SOC CHEM COMMUN 6 307-8' &
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& \BRIT 4 P' &
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& \MAY 24, 1972' &
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 & \CJ HEARSEY' &
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 TRIETHYLAMINE &
 & \K KONDO, N SONODA, ET AL' &
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 & \K KONDO, N SONODA, ET AL' &
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 & PREPARATION >
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 & \H HAGEMANN' &
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 BY PALLADIUM CHLORIDE &
 & \PM HENRY' &
 & \U.S. 2 P.' &
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- 0000721 * CARBONYLATION OF AROMATIC AZIDES, NITROSO, AND AZO COMPOUNDS
 WITH POLYMERIC PALLADIUM CARBONYL CHLORIDE, \PD-CO-CL'N &

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& \Z CHEM 1973, 13, 8, 288-9 GER' >
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& \NB FRANCO, MA ROBINSON' &
& PAT-01944746 GERMANY &
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& PAT-73-064048 JAPAN &
& \SEPTEMBER 5, 1973' >
- 0000724 * AROMATIC ISOCYANATES &
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& PAT-02334532 GERMANY &
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& \T YAMAHARA, T DEGUCHI, ET AL' &
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- 0000726 * AROMATIC ISOCYANATES &
& \T YAMAHARA, T DEGUCHI' &
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- 0000727 * AROMATIC ISOCYANATES &
& \T YAMAHARA, T DEGUCHI, ET AL' &
& PAT-74-018848 JAPAN &
& \FEBRUARY 19, 1974' >
- 0000728 * AROMATIC ISOCYANATES FROM NITROARENES &
& \T YAMAHARA, T TAKANO, ET AL' &
& PAT-75-052044 JAPAN &
& \MAY 9, 1975' >
- 0000729 * AROMATIC ISOCYANATES &
& \T YAMAHARA, S TAKAMATSU, ET AL' &
& PAT-02311092 GERMANY &
& \SEPTEMBER 20, 1973' >
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& \EH KOBER, WJ SCHNABEL' &
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WITH CO &
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- 0000733 * CATALYSTS FOR THE ONE-STEP PREPARATION OF 2,4 TOLUENE DIISOCYANATE FROM 2,4 DINITROTOLUENE &
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& \GER OFFEN 26 P.' &
& PAT-02165355 \USA' &
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- 0000734 * CATALYTIC PREPARATION OF AROMATIC ISOCYANATES FROM AROMATIC AZO AND/OR AROMATIC AZOXY COMPOUNDS &
& \SI TROTZ, TJ HURLEY, JR., ET AL' &
& \U.S. 4 P.' &
& PAT-03660458 &
& \MAY 2, 1972' &
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- 0000735 * NEW SYNTHESIS OF HETEROCYCLES BY THE REACTION OF AMINO ALCOHOLS OR AMINO THIOLS WITH CO IN THE PRESENCE OF SELENIUM &
& \N SONODA, G YAMAMOTO, ET AL' &
& \TETRAHEDRON LETT 1975, 24, 1969-72 ENG' >
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& \JJ MCCOY, JS YOO' &
& \U.S. 6 P.' &
& PAT-03714185 &
& \JANUARY 30, 1973' &
& PHOSPHINE >
- 0000737 * CYCLIC THIOCARBONATES &
& PAT-02202094 FRANCE &
& \MAY 3, 1974' >
- 0000738 * BENZAZOLES, BENZAZOLINONES, QUINOLINES, AND INDOLES &
& \AG MOHAN, RK MADISON' &
& PAT-02037998 GERMANY &
& \FEBRUARY 11, 1971' >
- 0000739 * INDAZOLONE DERIVATIVES &
& \TC KRAUS, MG NOACK' &
& PAT-03879416 \USA' &
& \APRIL 22, 1975' >
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& \Y IWASHITA, M SAKURABA, ET AL' &
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& \JUNE 12, 1973' >
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& \SYNTH COMMUN 5 2 131-5' &
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ON THE INITIATING EFFECT OF CO IN THE HYDROPOLYMERIZATION OF
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& \YT EIDUS, NI ERSHOV, ET AL' &

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CARBON-14 MONOXIDE AT LESS THAN 100 DEGREES &
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- 0000744 * FORMATION OF METHANE IN THE CO INITIATED CATALYTIC
HYDROPOLYMERIZATION OF ETHYLENE STUDIED WITH CARBON-14-LABELED CO &
& \GV ISAGULYANTS, NI ERSHOV, ET AL' &
& \IZV AKAD NAUK SSSR, SER KHIM 1973, 9, 2126-7 RUSS' >
- 0000745 * INTERPOLYMERS OF CO AND ETHYLENICALLY UNSATURATED
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& \K NOZAKI' &
& \U.S. 5 P.' &
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& \SEPTEMBER 10, 1974' &
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- 0000746 * TRICYANOPALLADIC ACID AS POLYMERIZATION CATALYST &
& \K NOZAKI' &
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& \K SHIRAYAMA, A SHIGA, ET AL' &
& PAT-75-034087 JAPAN &
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& \K SHIRAYAMA, A SHIGA, ET AL' &
& PAT-75-034044 JAPAN &
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& \JE GUILLET, HG TROTH' &
& PAT-02316697 GERMANY &
& \OCTOBER 11, 1973' >
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& \GYC CHAN, HJ WINTLE' &
& \J POLYM SCI, POLYM PHYS ED 1975, 13, 6, 1187-99 ENG' >
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& \B WEGEMUND, K WORSCHKECH, ET AL' &
& PAT-02433722 GERMANY &
& \JANUARY 29, 1976' >
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POLYMERIZATION OF ORGANIC COMPOUNDS. III - PLASMA POLYMERS OF
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& \H YASUDA, HC MARSH' &
& \J APPL POLYM SCI 19 11 2981-90' &
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& \S INOUE, H KOINUMA, ET AL' &
& \DIE MAKROMOLEKULARE CHEMIE 130, 1969, P210-220' >
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& \Y KOMATSU, Y FURUKAWA, ET AL' &
& PAT-75-016326 JAPAN &
& \JUNE 12, 1975' >
- 0000755 * SELECTIVE HYDROGENATION OF ALPHA, BETA-UNSATURATED CARBONYL AND NITRILE COMPOUNDS BY MEANS OF CO AND WATER IN THE PRESENCE OF RHODIUM CARBONYL COMPLEX &
& \N SAKAMOTO, T JOH, ET AL' &
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& \A YAMADA, M YANAGIDA, ET AL' &
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& \NOVEMBER 13, 1973' >
- 0000757 * SELECTIVE HYDROGENATION OF ALPHA, BETA-UNSATURATED CARBONYL AND NITRILE COMPOUNDS CATALYZED BY RESIN-SUPPORTED RHODIUM CARBONYL COMPLEXES &
& \T KITAMURA, T JOH, ET AL' &
& \CHEM LETT 1975, 3, 203-6 ENG' >
- 0000758 * RECOVERY OF NON-FERROUS METALS FROM OXIDE ORES AND CONCENTRATES &
& \RE SIEMENS, PC GOOC' &
& \U.S. 21 P.' &
& PAT-03929468 &
& \DECEMBER 30, 1975' &
& COPPER >
- 0000759 * REDUCTION OF IRON OXIDES POWDERS BY CO AT APPROXIMATELY 300 DEG &
& \CE BEAULIEU, A CLAVEAU, ET AL' &
& \CAN MET QUART 2 3 265-70' &
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& \M HUUSKA, M KOSKENLINNA, ET AL' &
& \THERMOCHIM ACTA 1975, 13, 3, 315-20 ENG' >
- 0000761 * THERMODYNAMIC EVALUATION OF THE POSSIBILITY OF THE REDUCTION OF SODIUM SULFATE BY PETROLEUM PYROLYSIS PRODUCTS &
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& \SB NAUCH ISSLED RAB IVANOV TEKST INST NO 9, 33-6' &
& \1971' &
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- 0000762 * CELLULOSE &
& \NS IMENITOV, GE GALPER, ET AL' &

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& \MARCH 1, 1973' >
- 0000763 * CARBONYL SULFIDE &
& \FR 9 P.' &
& PAT-02146664 FRANCE &
& \APRIL 6, 1973' &
& PRODUCTION >
- 0000764 * PREPARATION OF CARBONYL SULFIDE &
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APPENDIX A

CALCULATION AND OPTIMIZATION OF THE COST OF
TRANSPORTING HYDROGEN AND CARBON MONOXIDE
THROUGH A PIPELINE •

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CALCULATION AND OPTIMIZATION OF THE COST OF TRANSPORTING HYDROGEN AND CARBON MONOXIDE THROUGH A PIPELINE

The cost of transporting a gas through a pipeline is roughly a function of kind of gas to be transported, size of pipe to be used, pressure of the gas, cost of pipe, compressor, and labor. To operate a CO utilization plant economically the cost of gas transportation must be minimized. The cost study in the following section is aimed at identifying the cheapest way of transporting gas.

To compare the cost of various modes of transporting gas through a pipeline the following assumptions were made:

- 10^6 Btu/min of gas were to be transported through a pipeline 100 miles long.
- Gas to be transported was either CO or hydrogen.
- The source pressures of CO and hydrogen were assumed to be 14.7 psia.
- Two different delivery pressures of gas, 14.7 psia and 500 psia, were considered.
- The pipeline system was considered as a grass-roots facility.
- The cost for transporting gas through the pipeline system included: pipeline, compressor station, energy and labor cost.

General equations which minimize the gas transportation cost with respect to diameter of pipe and number of compressor stations follow.

The pipeline system can be depicted as follows:

Where 1, 2, n and t are numbers of compressor stations. P_0 is the pressure of gas fed to the first compressor. P_1 , and P_2 are pressure of gas at outlet and inlet of gas compressors, respectively. ℓ is the distance between two consecutive gas compressing stations.

1. Determination of Gas Pressure P_1

From Chemical Engineers Handbook, page 379 (3rd Ed.) equation (176)

$$w = \frac{\pi}{8} \sqrt{\frac{(P_1^2 - P_2^2) g_c D^5 M}{f \ell RT}} \quad (1)$$

where

w = weight rate of gas flow, lb/sec

P_1, P_2 = pressure at outlet and inlet of a compressor respectively, lb_f/ft^2

$g_c = 32.17 \text{ lb}_m \text{ ft}/(\text{lb}_f) (\text{sec}^2)$

D = diameter of pipe, ft

M = molecular weight of gas, $\text{lb}_m/\text{lb-mole}$

ℓ = distance between two consecutive compressor stations, ft

f = friction factor; in present study f is approximated by $f = 0.008D^{-1/3}$

R = gas constant = $1546 \text{ ft-lb}_f/(\text{lb-mole})(^\circ\text{F})$

T = temperature of gas, $^\circ\text{R}$

Rearranging and substituting ℓ by L/t into (1), where L is total length of pipe-line system and t is the number of compressor stations.

$$\left(\frac{8w}{\pi}\right)^2 = \frac{(P_1^2 - P_2^2) g_c D^5 M}{f \ell RT}$$

$$P_1 = \left[\left(\frac{0.008 LRT}{g_c M t D^{16/3}} \right) \left(\frac{8w}{\pi} \right)^2 + P_2^2 \right]^{1/2}$$

let

$$\alpha = \frac{0.008R}{g_c} \left(\frac{8}{\pi} \right)^2$$

$$P_1 = \left[\frac{\alpha L T w^2}{M t D^{16/3}} + P_2^2 \right]^{1/2} \quad (2)$$

2. Work required for each compressor

$$-W = \frac{k}{k-1} P_2 V_2 \left[\left(\frac{P_1}{P_2} \right)^{\frac{k-1}{k}} - 1 \right] \quad (3)$$

where

W = work, ft-lb_f/lb_m

$k = C_p/C_v$, C_p , C_v are heat capacity of gas at constant pressure and constant volume respectively

Since $P_2 V_2 = nRT_2 = RT/M$, equation (3) can be rewritten as:

$$-W = \frac{k}{k-1} \cdot \frac{RT}{M} \left[\left(\frac{P_1}{P_2} \right)^{\frac{k-1}{k}} - 1 \right] \quad (4)$$

let $\frac{k-1}{k} = \psi$ and substitute P_1 from (2) into (4)

$$-W = \frac{RT}{\psi M} \left\{ \left[\left(\frac{\alpha L T w^2}{M t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\} \quad (5)$$

3. Horse-power of compressor

$$H_p = \frac{wW}{550} = \frac{RTw}{550 \psi M} \left\{ \left[\left(\frac{\alpha L T w^2}{M t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\} \quad (6)$$

4. Energy requirement

$$E = 0.746 \times H_p \times N_h$$

where:

E = energy requirement, kW/hr/yr

N_h = operating hours, hr/yr

$$E = \frac{0.746 N_h R T w}{550 \psi M} \left\{ \left[\frac{\alpha L T w^2}{M t D^{16/3}} + P_2^2 \right]^{1/2} / P_2 \right\}^\psi - 1$$

$$= \frac{1.356 \times 10^{-3} N_h R T w}{\psi M} \left\{ \left[\frac{\alpha L T w^2}{M t D^{16/3}} + P_2^2 \right]^{1/2} / P_2 \right\}^\psi - 1 \quad (7)$$

5. Cost calculations

- The cost of pipe (CP) is calculated by

$$C_p = P_p \cdot (D)^{n_p}$$

where P_p = Cost of 1 in. pipe (\$0.48/ft for this study)

D = diameter of pipe, in.

n_p = diameter to cost correlation factor (1.2)

- The cost of compressor station (CS) is

$$C_s = (A_s + B_s) (1 + F_s) P_s (H_p)^{n_s} = \beta_s P_s (H_p)^{n_s}$$

where

A_s = amortization rate; 7% of compressor station cost/year

B_s = maintenance, 2% of compressor station cost/year

F_s = factor for compressor station installation including foundation and buildings, 50% of compressor cost.

$\beta_s = (A_s + B_s)(1 + F_s)$

- The cost of pipeline (CL) is calculated from the Chemical Engineers Handbook, page 384, (3rd ed.)

$$C_L = (A_p + B_p) (F_p + 1) P_p (D)^{n_p} L = \beta_p P_p (D)^{n_p} L$$

where

A_p = amortization rate, 1% of installed pipeline cost/year
(100 year life)

B_p = maintenance, 5% of installed pipeline cost/year

P_p = cost of 1 in. pipe (\$0.48/ft for this study)

F_p = factor for installation (including fittings), 50% of pipe

$\beta_p = (A_p + B_p) (F_p + 1)$

L = Total pipeline length (feet)

For a known amount of gas and T and fixed P_2 , P_s , P_E and P_{pr} the above equation simplifies to

$$C = \beta_p L P_p (D)^{n_p} + \left[\gamma \left\{ \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\}^{n_s} \right. \\ \left. + \theta \left\{ \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\} + N_{pr} P_{pr} \right] t$$

where

$$\gamma = \beta_s P_s \frac{RTw}{550 \psi M} n_s, \quad \delta = \frac{\alpha L T w^2}{M}, \quad \text{and } \theta = \frac{1.356 \times 10^{-3} N_h RTw}{\psi M}$$

Equation (3) is a function of D , diameter of pipe, and t , number of compressor stations. The optimum conditions can be found by setting $\frac{\partial C}{\partial D} = 0$ and $\frac{\partial C}{\partial t} = 0$ and solving D and t under these conditions.

where

$$\frac{\partial c}{\partial D} = \beta_p L P_p n_p (D)^{n_p-1} + \gamma t n_s \left\{ \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\}^{n_s-1}.$$

$$\psi \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^{\psi-1} \cdot \frac{1}{2 P_2} \left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{-1/2}.$$

$$\left(\frac{-16\delta}{3t} \right) (D^{-19/3}) + \theta t \psi \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^{\psi-1}.$$

$$\left(\frac{1}{2 P_2} \right) \left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{-1/2} \left(\frac{-16\delta}{3t} \right) (D^{-19/3})$$

- The cost of energy (CE) is

$$C_E = P_E \cdot E$$

where

P_E = unit cost of energy, \$0.015/kWh

E = energy required

- The cost of personnel (C_{pr}) is

$$C_{pr} = N_{pr} \cdot P_{pr}$$

where

n_{pr} = number of personnel

n_{pr} = salary of personnel, \$24,000/man-year

6. The total cost of transporting gas through a pipeline

$$\begin{aligned}
C &= C_\ell + (C_s + C_E + C_{pr})t = \beta_p L P_p(D)^{n_p} + \left[\beta_s P_s (H_p)^{n_s} + P_E E + N_{pr} P_{pr} \right] t \\
&= \beta_p L P_p(D)^{n_p} + \left[\beta_s P_s \left(\frac{RTw}{550 \psi M} \left\{ \left[\left(\frac{\alpha L T w^2}{M t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\}^{n_s} \right. \right. \\
&\quad + \frac{1.356 \times 10^{-3} N_h RTw}{\psi M} \left\{ \left[\left(\frac{\alpha L T w^2}{M t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\} P_E \\
&\quad \left. \left. + N_{pr} P_{pr} \right] t \right. \\
\frac{\partial C}{\partial t} &= \gamma \left\{ \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\}^{n_s} \\
&\quad + \theta \left\{ \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\} + n_{pr} P_{pr} \\
&\quad + t \gamma n_s \left\{ \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^\psi - 1 \right\}^{n_s-1} \cdot \psi \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^{\psi-1} \\
&\quad \left(\frac{1}{2 P_2} \right) \left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{-1/2} \cdot \left(\frac{-\delta}{D^{16/3}} \right) (t^{-2}) \\
&\quad + \theta t \psi \left[\left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{1/2} / P_2 \right]^{\psi-1} \cdot \left(\frac{1}{2 P_2} \right) \left(\frac{\delta}{t D^{16/3}} + P_2^2 \right)^{-1/2} \\
&\quad \left(\frac{-\delta}{D^{16/3}} \right) (t^{-2})
\end{aligned}$$

Some special cases with a single gas compressing station delivering gas pressure at 14.7 psia and 500 psia, and pipe diameters of 6 in., 8 in., 10 in., and 12 in. were calculated. Results of these calculations are presented in Tables A-1 and A-2 and Figures A-1 through A-5. Sensitivity analyses of changes

in cost factors, e.g., pipe, compressor, energy and labor were also performed. Results of these analyses are shown in Table A-3 and Figure A-6. For the purpose of comparison, the cost of transporting methane is also included in this study.

Since the molar heats of combustion of CO and hydrogen are almost the same, the volumes of gas to be transported in both cases are almost equal. These volumes are about three times that of methane. Due to the difference in molecular weights of the gases (CO = 28, hydrogen = 2), the energy required for transporting CO is higher than that of hydrogen. The energy requirements for transporting CO and hydrogen are both higher than the requirement for methane.

Our analysis indicates that the cost of a pipeline is a major portion of the total transportation cost, especially when the diameter of the pipe is large. When the pipe diameter is small (8 in. and 6 in.), the cost of energy becomes a predominant factor. In Case I, where delivery pressure was 14.7 psia, the minimum annual cost of hydrogen transportation is about $\$0.298/10^6$ Btu and the optimal pipe diameter is about 9 in.; the cost of CO transportaton was $\$0.405/10^6$ Btu and the optimal pipe diameter 12 in. In Case II, where delivery gas pressure was 500 psia, the minimum cost of transporting hydrogen in the range of conditions studied was $\$0.426/10^6$ Btu and the optimal pipe diameter 6 in.; the minimum cost of transporting CO was $\$0.483$ and the optimal pipe diameter 7.5 in. In both high and low pressure cases the cost of transporting hydrogen, on an equivalent Btu basis, is less than that of CO. The difference in delivered cost between the two gases becomes less significant when gas is delivered at high pressure because energy costs become the major cost factor.

TABLE A-1. Comparison of Pipeline Transportation Costs for Methane, CO, and Hydrogen

Case I: Initial and Final Pressure 14.7 psi

Diameter of Pipe, in.	Methane			
	12	10	8	6
Gas to be transported Btu/min	1×10^6	1×10^6	1×10^6	1×10^6
Volume of gas, ft ³ /min @ 32°, 14.7 psi	937.1	937.1	937.1	937.1
Wt of gas, lb/min	41.76	41.76	41.76	41.76
Gas pressure at compressor outlet, psi	34.86	52.2	94.2	201.3
Work, ft-lb _f /lbm	48.1×10^3	74.3×10^3	117.3×10^3	182.2×10^3
Power, hp	60.9	93.9	148.4	230.5
Energy, kWh/year	398.1×10^3	614.2×10^3	969.9×10^3	$1,506.6 \times 10^3$
<u>Cost</u>				
Pipeline, \$/year	112,480 (77.1) ^(a)	90,377 (70.4)	69,145 (60.6)	48,960 (47.0)
Cost compressor station \$/year	3,359 (2.3)	4,757 (3.7)	6,452 (5.7)	8,682 (8.3)
Cost of energy, \$/year	5,972 (4.1)	9,213 (7.2)	14,549 (12.7)	22,599 (21.7)
Cost of lab or \$/year	24,000 (16.5)	24,000 (18.7)	24,000 (21.0)	24,000 (23.0)
Total Cost \$/year	145,811 (100)	128,347 (100)	114,146 (100)	104,241 (100)

^(a) Numbers in parentheses are percentages.

TABLE A-1. (Continued)

Diameter of Pipe, in.	Carbon Monoxide		
	12	10	8
Gas to be transported Btu/min	1×10^6	1×10^6	1×10^6
Volume of gas, ft ³ /min @ 32°, 14.7 psi	2951.9	2951.9	2951.9
Wt of gas, lb/min	230.23	230.23	230.23
Gas pressure at com- pressor outlet, psi	132.6	214.9	388.2
Work, ft-lb _f /lb	88.1×10^3	116.2×10^3	156.2×10^3
Power, hp	614.9	810.5	1089.9
Energy, kWh/year	$4,018.2 \times 10^3$	$5,296.6 \times 10^3$	$7,122.5 \times 10^3$
<u>Cost</u>			
Pipeline, \$/year	112,480 (52.7)	90,377 (47.2)	69,145 (30.8)
Cost of compressor station \$/year	16,754 (7.9)	20,161 (9.4)	24,586 (10.9)
Cost of energy, \$/year	60,273 (28.2)	79,449 (37.2)	106,838 (47.6)
Cost of lab. \$/year	24,000 (1.2)	24,000 (11.2)	24,000 (10.7)
Total Cost \$/year	213,507 (100)	213,987 (100)	224,569 (100)

TABLE A-1. (Continued)

Diameter of Pipe, in.	Hydrogen			
	12	10	8	6
Gas to be transported Btu/min	1×10^6	1×10^6	1×10^6	1×10^6
Volume of gas, ft ³ /min @ 32°, 14.7 psi	2918.7	2918.7	2918.7	2918.7
Wt of gas, lb/min	16.26	16.26	16.26	16.26
Gas pressure at com- pressor outlet, psi	37.8	59.6	103.6	221.6
Work, ft-lb _f /lb	436.9×10^3	684.4×10^3	$1,056.9 \times 10^3$	$1,660.7 \times 10^3$
Power, hp	215.3	337.2	520.8	818.2
Energy, kWh/year	$1,405.9 \times 10^3$	$2,203.5 \times 10^3$	$3,403.4 \times 10^3$	$5,346.9 \times 10^3$
<u>Cost</u>				
Pipeline, \$/year	112,480 (67.8)	90,377 (57.0)	69,145 (43.4)	48,960 (28.2)
Cost of Compressor station \$/year	8,294 (5.0)	11,203 (7.1)	14,990 (9.4)	20,289 (11.7)
Cost of energy, \$/year	21,104 (12.7)	33,053 (20.8)	51,051 (32.1)	80,204 (46.3)
Cost of lab, or, \$/year	24,000 (14.5)	24,000 (15.1)	24,000 (15.1)	24,000 (13.8)
Total Cost \$/year	165,878 (100)	158,633 (100)	159,186 (100)	173,453 (100)

TABLE A-2. Comparison of Pipeline Transportation Costs for Methane, CO, and Hydrogen

Case II: Initial Pressure 14.7 psi, Final Pressure 500 psi

Diameter of Pipe, in.	Methane		
	12	10	8
Gas to be transported Btu/min	1×10^6	1×10^6	1×10^6
Volume of gas, ft ³ /min @ 32°, 14.7 psi	937.1	937.1	937.1
Wt of gas, lb/min	41.76	41.76	41.76
Gas pressure at compressor outlet, psi	500.9	502.6	508.6
Work, ft-lb _f /lb	277.2×10^3	277.6×10^3	279.0×10^3
Power, hp	350.9	351.3	353
Energy, kWh/year	$2,293.1 \times 10^3$	$2,296.0 \times 10^3$	$2,307.3 \times 10^3$
Cost			
Pipeline, \$/year	112,480 (61.7) ^(a)	90,377 (56.4)	69,145 (49.6)
Cost of compressor station \$/year	11,506 (6.3)	11,515 (7.2)	11,552 (8.4)
Cost of energy \$/year	34,397 (18.9)	34,395 (21.4)	34,610 (24.8)
Cost of lab, or, \$/year	24,000 (13.1)	24,000 (15.0)	24,000 (17.2)
Total Cost \$/year	182,383 (100)	160,287 (100)	139,307 (100)

^(a) Numbers in parentheses are percentages.

TABLE A-2. (Continued)

Diameter of Pipe, in.	Carbon Monoxide		
	12	10	8
Gas to be transported Btu/min	1×10^6	1×10^6	1×10^6
Volume of gas, ft ³ /min @ 32°, 14.7 psi	2951.9	2951.9	2951.9
Wt of gas, lb/min	230.23	230.23	230.23
Gas pressure at com- pressor outlet, psi	517	544.1	632.8
Work, ft-lb _f /lb	178.3×10^3	182.4×10^3	194.9×10^3
Power, hp	1243.6	1272.2	1359.7
Energy, kWh/year	$8,127.0 \times 10^3$	$8,314.1 \times 10^3$	$8,886.1 \times 10^3$
Cost			
Pipeline, \$/year	112,480 (39.4)	90,377 (33.9)	69,145 (27.1)
Cost of compressor station \$/year	26,858 (9.4)	27,271 (10.3)	28,513 (11.2)
Cost of energy, \$/year	121,905 (42.8)	124,712 (46.8)	133,337 (52.3)
Cost of lab, or, \$/year	24,000 (8.4)	24,000 (9.0)	24,000 (9.4)
Total Cost \$/year	285,243 (100)	266,360 (100)	254,995 (100)

TABLE A-2. (Continued)

Diameter of Pipe, in.	Hydrogen		
	12	10	8
Gas to be transported Btu/min	1×10^6	1×10^6	1×10^6
Volume of gas, ft ³ /min @ 32°, 14.7 psi	2918.7	2918.7	2918.7
Wt of gas, lb/min	16.26	16.26	16.26
Gas pressure at com- pressor outlet, psi	501.2	503.2	510.4
Work, ft-lb _f /lb	$2,476.2 \times 10^3$	$2,480.6 \times 10^3$	$2,496.6 \times 10^3$
Power, hp	1220	1222.3	1230.2
Energy, kWh/year	$7,973.1 \times 10^3$	$7,987.7 \times 10^3$	$8,039.1 \times 10^3$
<u>Cost</u>			
Pipeline, \$/year	112,480 (39.8)	90,377 (34.7)	69,145 (28.8)
Cost of compressor station \$/year	26,516 (9.4)	26,549 (10.2)	26,664 (11.1)
Cost of energy, \$/year	119,597 (42.3)	119,816 (46.0)	120,587 (50.2)
Cost of lab, or, \$/year	24,000 (8.5)	24,000 (9.1)	24,000 (9.9)
Total Cost \$/year	282,593 (100)	260,742 (100)	240,396 (100)
			224,548 (100)

FIGURE A-1. Gas Pressure, P , at Compressor Outlet

FIGURE A-2. Work Requirements for Transporting Gases

FIGURE A-3. Power Requirements for Transporting Gases

FIGURE A-4. Annual Cost of Gas Transportation. Case 1: Initial and final pressure 14.7 psi.

FIGURE A-5. Annual Cost of Gas Transportation (1×10^6 Btu/min).
Case 2: Initial pressure 14.7 psi and final pressure 500 psi.

TABLE A-3. Sensitivity Analysis for Relative Gas Transportation Costs

		Methane			
If pipe price increase 10%	1)	157.1×10^3 (7.7) ^(a)	137.4×10^3 (7.0)	121.1×10^3 (6.1)	109.1×10^3 (4.7)
	2)	193.6×10^3 (+6.2)	169.3×10^3 (+5.6)	146.2×10^3 (+5.0)	125.0×10^3 (+4.1)
If the compressor sta- tion cost increases 10%	1)	146.1×10^3 (0.2)	128.8×10^3 (0.4)	114.8×10^3 (0.6)	105.1×10^3 (0.8)
	2)	183.5×10^3 (0.6)	161.4×10^3 (0.7)	140.5×10^3 (0.8)	121.3×10^3 (1.0)
If energy costs increase 10%	1)	146.4×10^3 (0.4)	129.3×10^3 (0.7)	115.6×10^3 (1.3)	106.5×10^3 (2.2)
	2)	185.8×10^3 (1.9)	163.7×10^3 (2.1)	142.8×10^3 (2.5)	123.7×10^3 (2.9)
If energy costs decrease to \$0.007/kWh	1)	142.6×10^3 (-2.2)	123.4×10^3 (-3.9)	106.4×10^3 (-6.8)	92.2×10^3 (-11.6)
	2)	164.0×10^3 (-10.1)	142.0×10^3 (-11.5)	120.8×10^3 (-13.3)	101.2×10^3 (-15.7)
If the cost of Labor increases 10%	1)	148.2×10^3 (1.6)	130.7×10^3 (1.9)	116.5×10^3 (2.1)	106.6×10^3 (2.3)
	2)	184.7×10^3 (1.3)	162.7×10^3 (1.5)	141.7×10^3 (1.7)	122.5×10^3 (2.0)

^(a) Numbers in parentheses are percentages.

TABLE A-3. (Continued)

		Carbon Monoxide			
A-19	If pipe price increase 10%	224.8 x 10 ³ (5.3)	223.0 x 10 ³ (4.2)	231.5 x 10 ³ (3.1)	258.9 x 10 ³ (1.9)
		296.5 x 10 ³ (3.4)	275.4 x 10 ³ (3.4)	261.9 x 10 ³ (2.7)	270.0 x 10 ³ (1.8)
	If the compressor sta- tion cost increases 10%	215.2 x 10 ³ (0.8)	216.0 x 10 ³ (0.9)	227.0 x 10 ³ (1.1)	257.1 x 10 ³ (1.2)
		287.9 x 10 ³ (0.9)	269.1 x 10 ³ (1.0)	257.8 x 10 ³ (1.1)	268.4 x 10 ³ (1.2)
	If energy costs increase 10%	219.5 x 10 ³ (2.8)	221.9 x 10 ³ (3.7)	235.3 x 10 ³ (4.8)	269.0 x 10 ³ (5.9)
		297.4 x 10 ³ (4.3)	278.8 x 10 ³ (4.7)	268.3 x 10 ³ (5.2)	281.2 x 10 ³ (6.0)
	If energy costs decrease to \$0.007/kWh	181.4 x 10 ³ (-15.1)	171.6 x 10 ³ (-19.8)	167.6 x 10 ³ (-25.4)	173.9 x 10 ³ (-31.5)
		220.2 x 10 ³ (-22.8)	199.8 x 10 ³ (-25.0)	183.9 x 10 ³ (-27.9)	179.8 x 10 ³ (-32.2)
	If the cost of Labor increases 10%	215.9 x 10 ³ (1.1)	216.4 x 10 ³ (1.1)	227.0 x 10 ³ (1.0)	256.4 x 10 ³ (0.9)
		287.6 x 10 ³ (0.8)	268.8 x 10 ³ (0.9)	257.4 x 10 ³ (0.9)	267.6 x 10 ³ (0.9)

TABLE A-3. (Continued)

	Hydrogen			
If pipe price increase 10%	177.1 x 10 ³ (6.8)	167.7 x 10 ³ (5.7)	166.1 x 10 ³ (4.3)	178.3 x 10 ³ (2.8)
	293.8 x 10 ³ (4.0)	269.7 x 10 ³ (3.5)	247.3 x 10 ³ (2.9)	229.4 x 10 ³ (2.2)
If the compressor station cost increases 10%	166.7 x 10 ³ (0.5)	159.8 x 10 ³ (0.7)	160.7 x 10 ³ (0.9)	175.5 x 10 ³ (1.2)
	285.2 x 10 ³ (0.9)	263.4 x 10 ³ (1.0)	243.1 x 10 ³ (1.1)	227.3 x 10 ³ (1.2)
If energy costs increase 10%	168.0 x 10 ³ (1.3)	161.9 x 10 ³ (2.1)	164.3 x 10 ³ (3.2)	181.4 x 10 ³ (4.6)
	294.6 x 10 ³ (4.2)	272.7 x 10 ³ (4.6)	252.5 x 10 ³ (5.0)	236.9 x 10 ³ (5.5)
If energy costs decrease to \$0.007/kWh	148.2 x 10 ³ (-10.7)	141.0 x 10 ³ (-11.2)	131.9 x 10 ³ (-17.2)	130.7 x 10 ³ (-24.7)
	218.8 x 10 ³ (-22.6)	196.8 x 10 ³ (-23.5)	176.1 x 10 ³ (-26.8)	158.2 x 10 ³ (-29.5)
If the cost of Labor increases 10%	168.3 x 10 ³ (1.4)	161.0 x 10 ³ (1.5)	161.6 x 10 ³ (1.5)	175.8 x 10 ³ (1.4)
	285.0 x 10 ³ (0.8)	263.1 x 10 ³ (0.9)	242.8 x 10 ³ (0.9)	226.9 x 10 ³ (1.1)

FIGURE A-6. Sensitivity Analysis of Cost Factors in Gas Transportation

APPENDIX B

CATALYST POISONS

APPENDIX B

CATALYST POISONS

There are several catalytic chemical synthesis processes which could make good use of recycled waste carbon monoxide-containing gas streams. Other components of such waste gas streams may make usage of waste CO difficult due to their poisoning effect on the catalysts. The following is a list of known and suspected poisons for each of the catalysts which might be involved.

Ammonia Synthesis

- Water-gas shift $\text{H}_2\text{O} + \text{CO} \longrightarrow \text{H}_2 + \text{CO}_2$

There are two catalysts presently used in this process:

1. Iron oxide with a chrome oxide promoter is the higher temperature catalyst generally used above 350°C, and up to 500 psig. There are very few poisons for this catalyst. It is sulfur resistant. Although activity may be reduced up to 50 percent by 100 ppm sulfur, the deactivation is reversible by introduction of sulfur-free gas. Large quantities of halogen may poison the catalyst as may nitric oxide or acetylene. Contamination as low as 50 ppb of Hg, Mn or K will reduce activity and 50 ppb of phosphorus changes the specificity such that aldehydes are produced.
2. Copper-zinc oxide is a low temperature catalyst operated at 200-250°C. This high conversion catalyst (99.8 percent) can be used in a once-through type of process. According to the manufacturer this catalyst is poisoned by "just about everything". At the level of 0.2 ppm the catalyst will be inactivated by any of the following: any sulfur compound, any halogen and especially chlorine, Hg or P. Overheating will also destroy the catalyst. This catalyst does have a self-guarding capacity. The poisons are picked up so quickly that a deactivated zone develops at the head end of the catalyst bed, and the deactivated zone grows through the catalyst bed as more poison comes into the system. The end of the bed is effectively protected during the early stages of poisoning.

A new experimental catalyst has been patented by VPI and M. W. Kellogg. This low-temperature catalyst is a presulfided form of Cs or K acid salt and Co and/or Mo. The U.S. Patent 3,112,757 is held by Peter R. Rony and D. S. Newsome.

- Methanation $3\text{H}_2 + \text{CO} \longrightarrow \text{CH}_4 + \text{H}_2\text{O}$

This exothermic process operates at 300-400°C with 100-125 psig of pressure. The process is used to reduce the carbon oxide concentration of synthesis gas from about 2 percent to 2-3 ppm. Other processes such as the ammoniacal copper or cryogenic wash are used in place of this step in some plants. The most important methanation catalyst is nickel oxide on alumina with optional Mg or Cr oxides. It is known to be poisoned by sulfur compounds at 0.2 ppm or halogen compounds including HCl at 1 ppm. This poisoning is not reversible nor is the catalyst self-guarding. The catalyst can also be poisoned by fumes carried over from the CO₂ scrubber which often precedes the methanator. Phosphorus is probably not a poison.

The shift catalysts and the methanation catalyst are available from Girdler Catalyst Co.

- Ammonia synthesis $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

This process operates at 2,000-10,000 psig of pressure at 475°C. The most common synthesis catalyst is iron oxide with oxides of Al and K as promoters. Actually, the iron is reduced in the reaction leaving porous iron containing the promoters. Many poisons have been identified for this catalyst. It is poisoned by free and combined oxygen, for example, CO, CO₂, H₂O, NO₂, SO₂ and NO; but the effect is weaker at high temperature (515°C) than at low temperature (430°C). Free oxygen is only a temporary poison, whereas the combined forms are removed less easily, although they are reversible poisons. The most serious poisons are sulfur (0.1 percent), chlorine and phosphorus. Other known poisons are arsenic, bismuth, tellurium, selenium, and boron. Tests of the poisoning effect of some hydride compounds indicates the following order: P < As < Sb < W, with the relative strengths being 1:1:1.05:1.29. The ammonia synthesis catalyst is available from Haldor-Topsoe.

Phosgene Synthesis $\text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2$

Very little study has been done on the effects of impurities in the gases used in this process. Dried, filtered, essentially pure reactants are used. The activated charcoal bed would seem prone to poisoning. The exothermic reaction is stabilized at 200°C and 2 to 4 psig pressure.

Acetic Acid Synthesis $\text{CO} + \text{CH}_3\text{OH} \longrightarrow \text{CH}_3\text{COOH}$

Two catalysts are known for this process. The rhodium complex is used at low pressure and temperature (1,000 psi, 175°C) and the cobalt complex is used at high pressure and temperature (7,500 psi, 250°C). As with the phosgene synthesis little is known about poisoning effects on the catalyst. No poisons are normally found in the feedstock. Sulfur compounds have never been tested. Phosphorus and hydrogen are probably inert.

Oxo Reaction

The first reaction produces aldehydes which are converted to alcohols in the second.

A cobalt compound such as naphthanate, acetate, hydrate, oxide or carbonate is injected into the system where it is converted to cobalt hydrocarbonyl which acts as the catalyst. Sulfur does not affect this catalyst. Seventy percent conversion is achieved with catalyst concentrations of 3-5 percent. The exothermic reaction is operated at 150°C and 3,000 psig. All CO and carbonyl must be removed before the second step. In order for hydrogen to be recycled from the first step to the second it must first be sent through a methanation reactor.

Several catalysts can be used in the second reaction. These include 44 to 70 percent nickel on Kieselguhr, copper chromite and 20 percent cobalt oxide on alumina. These catalysts may be inactivated by sulfur. Since phosphorus is sometimes added to Ni and Co catalysts as an activator, little interference is foreseen from its presence as an impurity. Fluorides would probably fall

into the same category as chlorides as poisons. The effect of hydrocarbons or water is variable. Some processes have been run with up to 10 percent water and/or hydrocarbons without problems from contamination.

Methanol Synthesis $\text{CO} + 2\text{H}_2 \longrightarrow \text{CH}_3\text{OH}$

Methanol is made at 300°C and 3,750 psi over a zinc chromite catalyst. The catalyst is not very sensitive to common poisons, but sulfur is avoided because methylmercaptan could form. Chlorine and acetylene have also been reported as poisons. Reports also indicate that the presence of NO can cause formation of amines. One of the biggest problems with this catalyst is metal poisoning by iron, nickel and similar metals. The effect of fluorides or phosphorus is unknown.

A copper catalyst has also been used for methanol synthesis at low (750 psig) pressures. This catalyst is more active but also more easily poisoned. Sulfur compounds such as H_2S , COS, or CS_2 can deactivate the catalyst in concentrations as low as a few milligrams per cubic meter.

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