DE/PC/98055-715

TECHNOLOGY DEVELOPMENT FOR IRON F-T CATALYSTS

FINAL REPORT

prepared for
The U. S. Department of Energy
Pittsburgh Energy Technology Center

under
Contract No. DE-AC22-90PC90055

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August 1994

Patent clearance granted by
Chicago OPC on July 22, 1994.

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ACKNOWLEDGMENT

The authors express their gratitude to Dr. Jule Rabo and Prof. Dr. Hans Schulz for helpful discussions. Furthermore, Prof. Schulz generously furnished us with a copy of the three volume Schering report on the Fischer-Tropsch process.

Dr. Hayim Abrevaya was the principal investigator during the early stages of this contract and was available as a consultant throughout.

Dr. Lewis Liu, who was a co-op student with us, is responsible for the mathematical treatments which allowed calculation of α_1 and α_2 after the fashion of Satterfield. Furthermore, he did the work which allowed comparison of our data to previous worker's data in a known kinetic rate expression.

Tony Polak, then of UOP, wrote an in-house review of Fischer-Tropsch related surface science studies in 1982. This has been useful throughout this contract and particularly so as background in writing the final report.

Prof. Burt Davis and the other Fischer-Tropsch team members at the University of Kentucky as well as Professor Dragomir Bukur of Texas A & M University also were helpful and always willing to share data from their slurry phase Fischer-Tropsch experiments. The Air Products and Chemicals, Inc. team was very forthcoming and helpful during our participation in the Fischer-Tropsch

Demonstration run at LaPorte, Texas.

In addition to the undersigned, the Fischer-Tropsch team at UOP included at various times the following individuals: Dr. Hayim Abrevaya, Dr. Michael Quick, Dr. Alan van Til, Dr. Susan Lambert, Dr. Steven Bradley, Dr. Michelle Cohn, Frank Dobbs, William Targos, Elaine Schumacher, Sheila Adami, Robert Wasberg, Mark Heynis, Steve Bass and Kevin Kocis.

Finally, we acknowledge the team at DOE, both from the PETC, particularly Dr.'s Udaya Rao and Gary Stiegel, and Washington, D.C. offices for their helpful support during this work.

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1. OBJECTIVES

The objectives of this contract were twofold:

- I. Construct a pilot plant for preparing precipitated iron oxide F-T precursors and demonstrate that the rate of production from this plant is equivalent to 100 lbs/day of dried metal oxide.
- II. Prepare catalysts from these precipitates capable of achieving 88% CO + H₂ conversion with ≤ 5 mole percent selectivity to methane + ethane. A standard set of operating conditions was defined.

2. INTRODUCTION

This section is a brief summary of the Fischer-Tropsch (F-T) Process. It was written as a forward to the work done under this contract and was not meant to be a complete summary of all the work done in this area. Since Fischer and Tropsch discovered this process approximately sixty years ago hundreds of papers and patents have been written; a comprehensive summary of this area would be beyond the scope of this report. This section is biased in favor of the iron F-T catalyst since this contract is for iron catalyst development. Cobalt is the other common F-T catalyst. It is reviewed in the introduction section of the final report of DOE Contract No. DE-AC22-89PC89869; a contract to UOP for the development of cobalt F-T catalysts.

2.1 FISCHER-TROPSCH BACKGROUND

F-T is one of several processes which use synthesis gas ($H_2 + CO$) as feed. The current sources of synthesis gas are methane and coal. Synthesis gas is an expensive feed even when cheap methane or coal is available such as essentially valueless remote-site methane. This is due to the high capital cost of a synthesis gas plant. Fifty to seventy percent of the total cost of an F-T complex is due to the synthesis gas plant. Additionally, since F-T catalysts demand very pure feed, feed pretreatment can be very expensive as well. To stand these expenses F-T could only compete with high priced petroleum. In today's prices petroleum might have to reach thirty-five dollars a barrel or higher before F-T would be competitive even with a cheap feed for the synthesis gas plant.

F-T is a very non-selective process. A wide carbon number distribution of hydrocarbons and some

oxygenates are formed. Secondary processing is required to convert this multiplicity of products into fuels and chemicals. However, there are advantages to the F-T product. For instance, since the F-T hydrocarbons are essentially linear, a good quality diesel fuel product can be produced with a minimum of secondary processing.

F-T processing has enjoyed several brief periods of popularity. It was used in Germany during World War II to convert coal-derived synthesis gas into transportation fuels when the Allies cut off the Axis power's supply of petroleum. For a while after the war F-T development continued in Germany, mainly in Koebel's laboratory, and in the U.S. by the Bureau of Mines. Thereafter F-T work was scaled back everywhere but in South Africa which faced the continual threat of a petroleum embargo, but had a coal resource and historically cheap labor to mine it. As a result several generations of F-T reactors have been built in South Africa to process coal-derived synthesis gas. Although much of this work has not been published, some South Africans such as Dry have been active in the literature.

F-T enjoyed a second period of popularity in the mid-1970's after the Arab oil embargo. Research projects were then started as part of the worldwide syn-fuels effort at many academic, industrial and government laboratories; there are several reviews which cover this recent work.^{1, 2, 3, 4, 5} Although much of this effort was scaled back by the late 1980's some interest remains, particularly in the area of conversion of synthesis gas from remote-site methane. One large-scale F-T plant has been built to convert synthesis gas from such methane, namely Shell's Indonesian plant which uses tube reactors of narrow dimension to aid heat removal from the very exothermic F-T reactions. Over seventy thousand tubes divided between three reactor assemblies are used!

The Shell plant is an example of F-T by fixed bed processing which is also the type of processing used in the initial German plant in 1935. Fluidized catalyst beds (liquid and gas phase) have also been used. In liquid phase slurry processing part of the heavy products produced during F-T processing (wax) is retained in the reactor as a liquid to fluidize the catalyst under the influence of the reactant gas bubbles and to provide a heat transfer agent for the exothermic F-T reactions. This type of processing is called liquid phase Fischer-Tropsch (LPFT) processing.

In this contract the means to prepare commercial quantities of an iron-based LPFT catalyst were to be developed. Additionally, the catalyst was to meet certain performance targets, specifically it was to exhibit ≤ 5 mole % methane + ethane selectivity at 88% carbon monoxide + hydrogen conversion 2.4 NL/hr · g iron feed rate. Carbon number distribution among the F-T products is according to the Schulz-Flory distribution which means the amount of product at any carbon number, N, is related by a probability or chain growth number, α , to the amount at carbon number N-1. Because of the Schulz-Flory relation this contract's performance target is tantamount to development of a high wax-producing catalyst (low light product selectivity implies more product at high carbon numbers). The reason for a low methane + ethane target is that both of these products are of low economic value; they would probably have to be recycled to the gasifier. In many of the catalyst screening runs only conversions and light product selectivities were determined. Only occasionally were full carbon number range product analyses performed.

During this work feed was used which contained argon internal standard to aid calculations of conversions and selectivities according to Appendix 1. Analyses were performed by two on line gas chromatographs, data from one was used to calculate conversions and $C_1 \rightarrow C_4$ hydrocarbon selectivities and that from the other to calculate $C_2 \rightarrow C_4$ alcohol selectivities. Contact time plots were

sometimes made; in these cases contact times were calculated according to a method which is also outlined in Appendix 1.

2.2 THE SHIFT REACTION

Iron oxide-derived materials also catalyze the reaction of water with carbon monoxide to form hydrogen and carbon dioxide, the so-called shift reaction. This reaction proceeds at a comparable rate to carbon chain growth,⁶ in some cases considerably faster.² Since water is a product of the F-T reactions shift chemistry is observed during F-T processing. The resulting hydrogen is available to react with CO via F-T chemistry:

The practical significance of the overall stoichiometry above is that low hydrogen synthesis gas such as that from coal can be used without addition of extra hydrogen. Coal-derived synthesis gas has a hydrogen : carbon monoxide molar ratio of about 0.7 which is sufficient for the above stoichiometry ($\text{H}_2 : \text{CO} = 0.5$) with some hydrogen left over to form methane and alkanes which are not taken into account above. Methane-derived synthesis gas, on the other hand, exhibits a hydrogen : carbon monoxide molar ratio of two; cobalt-based catalysts which do not catalyze the shift reaction are most often used for such a feed.

2.3 REACTION MECHANISM

The currently favored F-T mechanism is, in fact, the original mechanism proposed by Fischer and Tropsch.⁷ It involves cleavage of carbon monoxide as the initiation step. This cleavage occurs at surface iron sites and results in the formation of iron carbides and iron oxides. The iron carbide then may build up to the main products of the F-T process which are paraffins and olefins by the steps of hydrogenation and insertion. Iron-bound methyl and methylene radicals thus may be formed from iron-carbide by hydrogenation. Chains may be formed by insertion of methylene radicals into the methyl-iron and alkyl-iron bonds.

Other mechanisms based on intact carbon monoxide have been proposed,^{8, 9} but are now out of favor. Although these mechanisms are out of favor, it is true that carbon monoxide can adsorb on metals intact or dissociated. Metals to the left of iron and cobalt in the periodic table adsorb carbon monoxide dissociatively whereas those to their right adsorb it intact.^{4, 10} Much of this knowledge is due to work with clean metal surfaces and the addition of carbon monoxide in quantities roughly needed to form a monolayer. However, a working catalyst might not be even closely approximated by such a surface. For instance, metals to the left of iron in the periodic chart do not catalyze the F-T reaction even though they can cleave carbon monoxide. Their lack of F-T activity seems to result because a surface coating of metal oxide is formed which is thermodynamically stable under F-T conditions and inactive for the cleavage of additional carbon monoxide. Metals to the right or below iron, cobalt and nickel, particularly palladium, can be active as methanol synthesis catalysts. This, of course, implies that carbon monoxide reacts with hydrogen as an intact molecule—yielding methanol via hydrogenation.

The non-dissociative F-T mechanism became firmly entrenched in the late 1940's, in large part due to Emmett and co-workers. They provided what at first appeared to be a formidable thermodynamic argument refuting the dissociative mechanism. It was based on data for the formation of hydrocarbons from hydrogenation of bulk phase metal carbides including those of iron and nickel.^{11, 12, 13} Emmett et. al. calculated equilibrium constants for this type of transformation from known free energies including those of bulk phase metal carbides. At normal F-T pressures and temperatures these constants predicted only minimal conversion to hydrocarbons.

The non-dissociative mechanism was in vogue until the late 1970's when fresh theories and evidence supporting the dissociative mechanism were advanced by Rabo and co-workers,^{14, 15} and later by many others as well. Araki and Poniec¹⁶ and Wentrcek and co-workers¹⁷ supported a dissociative mechanism for methane formation over nickel surfaces at about the same time. The thinking by these workers was that bulk phase metal carbides should not be invoked to explain transformations occurring on a surface.

Somewhat later rapid dissociation of carbon monoxide on the catalyst surface in the presence of hydrogen became a key aspect of the theory proposed by Biloen, Helle and Sachtler to explain how hydrocarbons are formed by F-T catalysts.¹⁸ Their acceptance of this theory was based on work they did with metals containing surface coverages of ^{13}C formed by disproportionation of ^{13}CO to ^{13}C and $^{13}\text{CO}_2$ at 523°C and 0.5 bar. (This is the "Boudouard" reaction which is also known to occur during activation and use of Fischer-Tropsch catalysts. Although normally not a problem, care must be taken, particularly during catalyst activation with carbon monoxide, that this reaction does not produce excess carbon with a resultant loss in catalyst activity.)

With a measured amount of ^{13}C Biloen, et. al. prepared carbidic materials that were active when reacted with successive batches of $^{12}\text{CO}/\text{H}_2$ each sufficient to consume 20% of the ^{13}C . They found hydrocarbon products which contained ^{13}C under conditions where the carbidic carbon had been demonstrated not to equilibrate back to carbon monoxide. Thus it appears that the surface ^{13}C reacted with hydrogen, putatively forming $^{13}\text{CH}_2$ and $^{13}\text{CH}_3$, the latter of which can form $^{13}\text{CH}_4$ via reaction with hydrogen and higher ^{13}C hydrocarbons via insertion of $^{13}\text{CH}_2$. Rabo and others invoked the dissociative mechanism at about the same time as Biloen, et. al.^{14, 19, 20, 21} The small amounts of oxygenates found in F-T products could arise according to this mechanism by insertion of carbon monoxide into a growing chain, presumably this would be a chain termination step.⁵

Petit and Brady and later Bock have explored the dissociative mechanism by generating carbenes on the surface of F-T metals.^{22, 23, 24} Petit and Brady showed that decomposition of diazomethane in the absence of hydrogen on F-T metals or in the presence of hydrogen on metals that cannot adsorb it dissociatively results in ethylene as the only product. However, decomposition of diazomethane on F-T metals in the presence of hydrogen leads to a normal F-T product slate.

The dissociative mechanism has been criticized recently by Henrici-Olive and Olive, particularly with regard to the relevance of the Petit experiment.^{25, 26} However, Smutek has defended it while emphasizing this experiment.²⁷

Hoffmann and co-workers have reviewed the mechanistic work done up to the mid-1980's and provided an extended Huckel model for F-T catalysis based on the dissociative mechanism.²⁸

Hoffmann treats all of the steps in this mechanism not just the initial carbon monoxide cleavage. He discussed, for instance, the mobility of carbon intermediates on the surface and how that can

relate to the F-T products. Surface mobility is related to d-band filling. The chain propagation step can be visualized as migration of an alkyl group and/or methylene into close proximity allowing facile coupling (chain growth). Hoffmann has made strides toward understanding the theoretical underpinning of F-T catalysis. His theory is predictive, for instance, the differences in product distribution between Co (shorter chains) and Fe (longer chains) is due to different carbon fragment mobility as predicted by the different d-band filling in these two metals.

Biloen²⁹ and others have continued to elucidate the F-T mechanism through use of ¹³CO. This recent work employs alternate pulses of ¹²CO/H₂ (D₂) and ¹³CO/H₂ (D₂) with the same CO : H₂ ratio, the so-called transient response isotopic tracer experiment.^{30, 31} Information regarding the rates of the various reactions in the F-T mechanism can be obtained. For instance, the change in rate constants for propagation and chain termination going from C₁ → C₃ have been estimated for a cobalt catalyst.²⁹ These workers found the rate constant for propagation decreased from 0.045–0.025 s⁻¹ and that for termination increased from 0.02 → 0.04 s⁻¹. Mims, et. al. have also employed this method to obtain values for rate constants for both iron and cobalt catalysts.^{32, 33} Krishna and Bell have reviewed this work and presented recent results allowing estimations of activation energies for chain propagation and termination using a ruthenium on titania catalyst.³⁴ They find chain propagation and termination to have activation energies of, respectively, 8 and 20 kcal/mole. Qualitatively, this is not a surprising result because it is known that lower molecular weight products are favored at higher temperatures.

Attempts have been made to apply transient state kinetics to determine F-T rate constants.^{35, 36, 37} This work has been done to try to understand why the turnover numbers for F-T are as much as two orders of magnitude lower than other metal-catalyzed reactions such as hydrogenation.⁸

Dautzenberg³⁶ pulsed synthesis gas followed by hydrogen over a ruthenium catalyst. He adjusted the pulse times and was able to estimate rate constants for the propagation and termination steps. The data in Figure 147 are from this work. Besides the kinetic information, this experiment illustrates the potential of using pulse feeding to change the product distribution obtained from a given catalyst. Clearly, it is possible to obtain products which are on average lower in molecular weight from short pulses. From the kinetic analysis Dautzenberg concludes that the low turnover numbers result from low kinetic rates per site rather than the alternative which is only a fraction of the exposed metal atoms being active (low Taylor number). However, Biloen and Sachtler³⁵ raise questions about underlying assumptions made by Dautzenberg which should be cleared up in future studies.

In summary, the dissociative mechanism now seems to be the accepted one for F-T processing. In addition, Hoffmann's theory is now available which attempts to understand the factors controlling all of the mechanistic steps including the polymerization steps. This is, so far, a theory based on simple assumptions. For instance, the theory uses a metal slab model which assumes a flat surface with atom spacing characteristic of a crystal face. The slab is free of surface bonds other than the surface carbon ones required to build up F-T products. The actual iron F-T catalyst is known to contain metal-oxygen and metal-carbon bonds on the surface. Furthermore, an actual F-T catalyst, iron or cobalt, almost certainly has an irregular surface with "steps" and "kinks" which will probably strongly affect the catalyst performance. However, Hoffmann's theory is comprehensive in that it attempts to cover all steps of the F-T process not just the "dissociative" step. Additionally, it does so in an understandable fashion while using the strong and well-developed logic of molecular orbital theory. It should be expanded not discarded.

The work done to understand the mechanism of the F-T process has produced further insights into how metal crystallites actually function as catalysts and how electronic changes across a row of the periodic chart can pronouncedly affect product selectivity. This can allow powerful insights into the nature of catalysis when coupled with an understanding of what the actual surface layer is on such crystallites. For instance, as Rabo has pointed out,^{14, 15} metals to the left of iron in the periodic table form a stable surface oxide. Once the oxides are formed in the initial stages of processing under F-T conditions the surface can no longer accept oxygen, even under reducing conditions. The surface thus becomes ineffective for cleaving the carbon-oxygen bond. Metals below and to the right of iron, cobalt and nickel (e.g. palladium) are reduced but lack the ability to cleave carbon monoxide..Methanol can result from them under F-T conditions. Iron exists under F-T conditions with both iron-carbon and iron-oxygen bonds on the surface. It is an F-T catalyst as well as a shift catalyst. Cobalt is one element to the right of iron in the periodic chart. Under F-T conditions its surface contains no detectable cobalt-oxygen bonds. Cobalt is an F-T catalyst but not a shift catalyst perhaps because it is not partially oxidized to cobalt oxide. It apparently is in the metallic state during F-T catalysis, probably with a surface covering of carbon. Furthermore, it is intrinsically more selective to methane and other light hydrocarbons than iron. Nickel is one element to the right of cobalt; it also is in the metallic state under F-T conditions. Under F-T conditions its surface also probably contains carbon. Nickel can catalyze the formation of hydrocarbons, but only forms ones heavier than methane with difficulty. It is also not a shift catalyst. One strength of Hoffmann's theory is that it provides an explanation for the difference in carbon number selectivities resulting from catalysts across the row: iron → cobalt → nickel. Presumably this theory can also be extended to explain why stable surface carbon-oxygen bonds are favored going from right to left across this row.

2.4 CARBON NUMBER SELECTIVITY IN LIQUID-PHASE FISCHER-TROPSCH PROCESSING

The wide range of carbon number products in F-T processing can be understood in terms of the mathematics first used by Schulz³⁸ and Flory³⁹ for condensation polymerization. Thus if a complete product work-up is performed during F-T processing and if a plot is made of log selectivity to each carbon number vs. carbon number, a straight line (single alpha case) or a hyperbolic curve appearing to result from two straight lines (so-called double alpha case) results. Plots of the above type are customarily called Schulz-Flory or Anderson-Schulz-Flory plots. Alpha (α) is the slope of the straight line(s); in Schulz-Flory kinetics it is the probability of a carbon chain of n atoms growing to one of $n + 1$ carbon atoms. Until recently most F-T data was presented as being of the single α type, however, it now appears that most, if not all, F-T catalysts produce the double α type of product distribution, certainly, in LPFT double α appears to be the norm. It is possible that early workers sometimes, at least, reported single α behavior because the breakpoint was at a high carbon number, requiring a complete product analysis to "see" the breakpoint. Such product analysis are facilitated by modern analytical techniques that were not available when the early F-T work was done. Catalysts which are very selective to methane and other light products can produce a product distribution which at least gives the appearance of being single α in nature since undetectable amounts of heavy materials may be formed.

The recent Ph.D. thesis of Yates⁴⁰, who was a student of Satterfield's at the Massachusetts Institute of Technology, contains a review of the experimental evidence for double α behavior. For instance, the first note of it appears to have been at a German pilot plant in 1943 during the "Schwarzheide tests". However, this data was not widely circulated and explanations for the double alpha product

distribution first started to appear years later. For instance, in 1983 Koenig and Gaube⁴¹ theorized it to be due to two different catalyst sites, one promoted by potassium and one not. Later, however, Dictor and Bell⁴² and Satterfield⁴³ observed the double alpha phenomenon with potassium-free catalysts.

Novak and co-workers^{44, 45} have also presented a two active site mechanism, one a condensation site and the other a cracking site. However, Yates points out that Schulz⁴⁶ and Pichler and Schulz⁴⁷ had earlier determined that cracking does not occur significantly on iron or cobalt F-T catalysts.

There is an alternate explanation for the double α effect. Satterfield's group⁴⁰ and Iglesia, et. al. at Exxon⁴⁸ propose that this effect is due to two chain growth processes. One of them is the historic one which involves carbon atom insertions into a growing chain. The other is growth by readsorption of product alkenes followed by their incorporation into chains. Although alkenes are primarily hydrogenated upon readsorption there was ample evidence prior to the mechanistic ideas of Satterfield's and Iglesia's groups that alkenes, particularly ethylene and to a lesser extent propylene and 1-butene can initiate and terminate chain growth.^{46, 49-51} There was also some evidence⁴⁶ that ethylene but not propylene can propagate growing chains as well. The basic concept addressed by Satterfield's and Iglesia's groups is the same, but Iglesia theorizes that alkene participation is related to fugacity implying more participation by higher molecular weight alkenes than Satterfield's and the historic experiments above might imply. It is known that most of the heavy F-T products are alkanes not alkenes, implying that the heavy products are the most strongly readsorbed and are reactive in, at least, the hydrogenation reaction.

Satterfield and his students have developed a mathematical model for the double α case.^{40, 52} It is

not dependent on a given double α mechanism. Included is a nonlinear regression method to assign values called α_1 and α_2 to the hyperbolic curve. These two constants roughly correspond to the values α_1 and α_2 that result from simple linear regression analysis of the apparently straight-line parts of the hyperbola. Yates reports, however, that the linear regression α 's are in error by 5-10% compared to the nonlinear α 's even if the only data used is from several carbon numbers away from the breakpoint. Satterfield, et. al's. method also reports a value X_i which can be likened to a breakpoint, but it can be a fractional number such as 9.4. During this contract a modified form of Satterfield's nonlinear regression analysis was used to calculate values for α_1 , α_2 and X_i (Appendix 2).

No catalyst or set of operational conditions have been discovered that allow good control of carbon number selectivity during F-T processing with iron or cobalt catalysts. Except for methane, it is not possible to make a single carbon number product such as only C_4 's or even a fairly narrow carbon range product such as only $C_4 - C_6$. To date changing carbon number selectivity during F-T processing only means changing the magnitude of α , for instance, a change in catalyst composition can shift the product distribution from one that is biased toward low molecular weight products to one that is biased toward higher molecular weight ones or vice versa. However, regardless of the catalyst both high and low molecular weight products will be formed.

Conversion of synthesis gas to C_1 products with other metal catalysts is also possible. For instance, very high methane selectivities can be obtained using a nickel catalyst and very high methanol selectivities can be obtained, for instance, with a palladium catalyst.¹⁴

During this contract Schulz-Flory plots were made when full carbon number range analyses were

performed. However, this is a very time-consuming process and was not done in a routine fashion. Schulz-Flory plots are important because there have been reports that C_1 and C_2 can fall above or below the Schulz-Flory line with some catalysts. This implies that these products can be "uncoupled" from the mathematical formalism of condensation polymerization. Lower levels of methane and/or ethane than predicted by Schulz-Flory would be an extremely important observation considering the objectives of this contract.

2.5 OTHER FISCHER-TROPSCH SELECTIVITIES

F-T processing is highly selective in one respect: the carbon chains are primarily unbranched. This is consistent with chain growth via sequential carbon atom insertions into an iron-carbon bond, with only a small number of insertions by $> C_1$ species. Only low levels of cyclic and aromatic products are formed.

Most of the heavier F-T products are saturated molecules; alkenes can be prominent among the low molecular ones. Of the two most studied F-T catalysts (Fe and Co), iron is more prone to form alkenes than Co. With some iron catalysts, at least, the extent of reduction of iron appears to alter the ethylene/ethane ratio, but not the carbon number selectivity at low conversion. Specifically, more ethylene results from the more highly reduced catalyst (3 vs. 63% iron reduction).⁵³ Incorporation of manganese sometimes improves the selectivity to alkenes in the low molecular weight products and sometimes doesn't.⁵⁴⁻⁶⁶ Operation of an iron/manganese catalyst at low pressure (atmospheric), 420° C and a feed rate of 120 cc/cc catalyst/hour has resulted in 38.3% carbon monoxide conversion and a high aromatics yield of 18%.⁶⁶ Zinc is also purported to favor alkenes in the low carbon number products.⁶⁷⁻⁶⁹

2.6 DESCRIPTION OF THE IRON FISCHER-TROPSCH CATALYST

In its usual manifestation the iron catalyst is unsupported. It is usually furnished as iron oxide, apparently even the slag from iron ore processing may be used as catalyst. The iron oxide catalyst precursor can be reduced (activated) in several ways including pretreatment with the synthesis gas feed itself. Other reductants such as carbon monoxide may also be used. Activation temperature and pressure may be the same as the operating temperature or different. Precursor activation can affect the catalyst activity and α .

Historically, the most important metal adducts for iron F-T catalysts are copper, potassium and silicon. Copper aids the reduction of iron oxide and potassium affects both catalyst activity and selectivity. When copper is used care is taken to get a good distribution of it throughout the bulk iron oxide, for instance, by co-precipitating it with iron. Potassium, on the other hand, is usually added to an iron-copper material in a separate step, for instance, by surface impregnation.

The affect of alkali, particularly potassium, was discovered very early by Fischer and Tropsch.⁷⁰ In their work powdered iron-copper compositions were used which resulted from decomposition and ignition of metal nitrates. Potassium was added separately as potassium carbonate. Catalyst activity increased with increasing potassium level, but so did the catalyst deactivation rate. Later, Pichler studied catalysts resulting from potassium carbonate addition to iron-copper oxides.^{71, 72} Tests were two months long at 235° C and 15 atm. No activity change was noted in going from 0 to 0.25% potassium. Greater than 1% potassium resulted in less active catalysts. As the potassium level was increased the selectivity to wax and oxygenates increased. More recently, Anderson has reviewed the affect of alkali promotion.⁷³ In this later work the activity increase and higher wax

selectivity due to potassium were confirmed.

Although the material furnished to an F-T reactor is best described as unsupported iron oxide with minor metal adducts, it is sometimes called a supported catalyst. This is because silica can be added to give the catalyst structural integrity. The Ruhr catalyst (4.8 wt% silicon) is an example of such a material; it was evaluated as a reference during the current work. Such catalysts are not supported in the usual sense because silicon is usually added during precipitation of the iron oxide, in other words the catalyst does not result from surface impregnation onto silica. Furthermore, regardless of the method of preparation, the level of silica is lower than it would be from impregnation onto silica. In the current work a few catalysts were prepared by coprecipitating low levels of silicon with iron and copper.

Although the iron F-T catalyst is reduced during activation it is not easily described. For instance, there is good evidence that some iron oxide remains in the working catalyst, although the carbon chain growth (F-T) sites appear to involve carbidic iron. There are many iron carbides known and more than one of them have been observed in functioning F-T catalysts, for instance, by Moessbauer spectroscopy. Many workers believe the iron F-T catalyst has more than one catalytic site. These sites could all be carbidic iron sites, each in a different steric and/or electronic environment, or they could be more complex. For instance, more than one iron could be required per site, perhaps with a mixture of iron-carbon and iron-oxygen bonds.

Some theorize that the shift reaction sites, on the other hand, are at places where there is oxidic iron because such sites might aid transfer of oxygen to carbon monoxide. In support of this, the cobalt F-T catalyst is fully reduced during use with no evidence of a cobalt oxide phase, this catalyst does

not catalyze the shift reaction. The possibility exists, therefore, that the F-T and shift sites are different, with one being essentially oxidic and the other carbidic. However, since the reduction and oxidation of carbon monoxide both involve transfer of oxygen atoms it is also likely that in both cases at least transitory iron oxygen bonds are present.

Attempts have been made to learn more about the mechanism of the F-T reactions through studies of the interaction of carbon monoxide and/or hydrogen with clean metal surfaces. Although such surfaces are not the same as an actual functioning F-T (iron oxide/carbide) catalyst useful knowledge may be obtained. For instance, hydrogen adsorption on Fe(100) is affected by potassium: although with and without potassium there are two desorption states (β_1 and β_2) and the total hydrogen coverage does not change, potassium does cause desorption temperatures to increase by about 30° K.⁷⁴ A similar finding of a 30-40° K increase was made for the Fe(111) surface. Separate work confirmed that the sticking probability and binding energy for hydrogen increases linearly as a function of potassium coverage.⁷⁵ Potassium was also found to strengthen the carbon monoxide surface bond (opposite to the affect of carbon, oxygen and sulfur) and to increase the amount of dissociated carbon monoxide. There is also some evidence that potassium can create new carbon monoxide adsorption sites.⁷⁶

It is also clear from the surface studies that the more open crystal faces of a given metal tend to be more active for carbon monoxide dissociation. Work with tungsten, for instance, illustrates carbon monoxide dissociation at 300°K on the tightly packed W(110) surface, but below 200°K on the more open W(100) surface.^{77, 78}

Work function changes have also been measured for promoters such as potassium. Low ionization

potential materials, e. g. alkali metals, donate electron density to a transition metal causing a decrease in the transition metal work function (increased electron density). This effect continues to increase with increasing coverage approaching the work function of the covering material. Specific examples for iron⁷⁹ and nickel⁸⁰ are available. The amount of change in work function follows the ionization potential of the covering material, lower ionization potential (better electron donating) materials are more effective at lowering the work function. The ionization potentials of the alkali metals generally decrease with increasing atomic number.

Metal work function increases are noted upon adsorption of hydrogen or carbon monoxide, indicating loss of electron density from the metal with a resultant addition of electron density to the adsorbed gas. Blyholder's model of CO adsorption is usually used to rationalize how the metal influences carbon monoxide upon adsorption.⁸¹ According to Blyholder electrons from the surface are donated into an antibonding carbon-oxygen bond thus causing this bond to be weakened. At the same time the metal-carbon bond is strengthened resulting in facile carbon-oxygen bond cleavage.

Care must be taken in using the results of experiments with clean metal surface planes to interpret what happens on the surface of a functioning catalyst. However, this is a rapidly growing field of interest with ever-increasing sophistication. For instance, one historic criticism has been that clean metal surface planes do not approximate an actual metal crystallite which can exhibit an irregular surface of "steps" and "kinks". However, Somorjai and others have been actively investigating clean but irregular surfaces.

It is also known that all F-T catalysts result from paramagnetic or ferromagnetic materials,

however, there are many such materials which do not produce active F-T catalysts (Figure 2). The electronic properties associated with the metal d orbitals are important in determining the metal's magnetic properties and probably are also important for F-T catalysis.²⁸ Magnetic measurements of actual iron-based catalysts have been performed during this contract, but more experimental and theoretical work is required.

2.7 CLUSTERS AS CATALYST ANALOGIES

Muetterties believed comparisons could be drawn between known metal clusters and intermediates formed catalysis.⁸² Clusters have played a role in understanding homogeneously-catalyzed hydroformylation. However, they have so far only contributed to an understanding of the first step F-T mechanism.

Metal clusters are multimetallic, ligand-stabilized complexes which exhibit metal-metal bonding. Just after the work of Biloen and the others Muetterties reviewed mechanistic aspects of carbon monoxide hydrogenation, specifically with regard to possible analogies between metal clusters containing carbon monoxide and potential reduction intermediates such as iron carbides.⁸³ He cited known metal carbonyl clusters, particularly those of iron and cobalt which might be used as models for intermediates in reactions such as those occurring during Fischer-Tropsch synthesis. For instance, $[\text{Fe}_4(\text{CO})_{13}\text{H}]$ contains one carbonyl simultaneously bonded to two iron atoms, similar perhaps to a surface carbon monoxide species prior to carbon-oxygen bond cleavage. Another cluster, $[\text{CFe}_5(\text{CO})_{15}]$, contains a carbidic carbon which exists below a basal plane defined by four of the five iron atoms in the cluster. Such clusters might be relatable to the carbide species of Biloen. Complexes containing other ligands, notably cyclopentadienyl, in addition to carbon

monoxide and which might be analogies for F-T intermediates include the bridged complex of manganese: $\text{Cp}(\text{CO})_2\text{Mn}\{\text{CH}_2\}\text{Mn}(\text{CO})_2\text{Cp}$. The methylene bridges a manganese-manganese bond. Such complexes and their possible relation to carbon monoxide hydrogenation including F-T have been reviewed.^{84, 85} However, at the time of the Muettert's review there were no examples of cluster complexes which could be converted from one hydrogenation intermediate analog into another.

The field of cluster analogies has been reviewed again recently by Gates.⁸⁶ He cites work of Chisholm, et. al.⁸⁷ who have discovered a dissociative reaction of carbon monoxide with a tungsten alkoxide complex. The new complex contains both oxidic and carbidic tungsten atoms. Although this is similar to what probably results on a surface when carbon monoxide dissociates, it is not yet an example of a cluster-containing carbon monoxide which can be converted into one with dissociated carbon monoxide. With this cluster initial carbon monoxide bonding must be slow compared to bond cleavage, isolation of the initial complex has not yet been described.

Gates compares Chisholm's work to that of Yates, et. al. who examined the reaction of carbon monoxide on a molybdenum surface.⁸⁸ Yates was able to show that carbon monoxide adsorbs intact at a low temperature but converts to molybdenum oxide/carbide at higher temperatures.

Gates points out that the initial interaction of a reactant with a cluster can be slow compared to reaction with a clean metal surface because the former requires a coordinatively unsaturated cluster. This, in turn, usually means removal of a ligand from a coordinatively saturated precursor which can be slow. Gates says that in a working catalyst reactants and products themselves can fill the role of the departing ligand in a cluster, perhaps making the cluster analogy closer to a real catalyst

than the clean metal analogy.

The cluster analogy for F-T chemistry has been very slow to develop. Clusters are not yet known that can demonstrate even one step in a carbon dioxide reduction process, although carbon monoxide complexation—> cleavage undoubtedly does occur in Chisholm's example. Furthermore, the cluster work to date has been concentrated on finding clusters which model only the initial steps of the carbon monoxide reduction processes. To be helpful in understanding F-T catalysis this work must eventually shed light on the important later steps which determine carbon number selectivity. The goal should be clusters which demonstrate how to obtain a very narrow carbon number distribution such as C_5 to C_{10} .

However, if Hoffmann is correct in thinking about F-T catalysis in terms of extended molecular orbital theory of a several atom thick metal slab there is an even more serious problem with the cluster analogy. Namely, how can the d electrons in a few metal atoms in a cluster ever mimic the behavior of the d electrons in an extended group of metal atoms? According to Hoffmann changes in the d-band electronic state influence the degree of polymerization during F-T synthesis. As stated above, understanding how to control the degree of polymerization should probably be the key objective of future F-T research.

2.8 FISCHER-TROPSCH REACTORS

Commercial F-T plants have traditionally used packed or fluidized bed reactors. In both cases the product liquids and gases are removed from the reactor as fast as they are formed. Provisions such as narrow tube reactor geometry must be provided to remove heat from the very exothermic F-T

reactions. Slurry liquid phase processing is a newer concept although Koebel did seminal work on it in the 1940's and early 1950's at the Rheinprussen Corporation plant at Hamburg Niederrhein, Germany. The driving force behind its development is the ability of the liquid phase to act as a heat transfer agent to remove heat from the reactor. F-T processing is very exothermic.

The first F-T plant was built in Germany in the 1930's. It had a fixed-bed reactor full of catalyst pellets and was operated between 200 and 270° C.⁸⁹ Due to the high exothermicity of the F-T reactions, precise catalyst temperature control was impossible. This resulted in shortened catalyst life. The product liquids were approximately a 50 : 50 mix of naphtha and higher boiling fractions. The most recent fixed-bed plants are in South Africa; they employ Arge reactors which use high catalyst loadings and high space velocities. The product liquids are about 40% naphtha with the balance heavier.

The M.W. Kellogg Co. has developed a type of fluidized-bed reactor called an entrained-bed reactor. It is used in the South African Synthol process. In it the catalyst and syn gas contact at the bottom of the reactor and proceed up together at 300-335° C. Cyclones separate products and catalyst; boilers are used to remove heat. The South Africans have developed two generations of Synthol reactors, Synthol I and II. Synthol II resulted from a cooperative effort with Badger Engineers Inc. to rectify problems associated with Synthol I.⁹⁰ The Synthol reactors are operated to produce a light product which is about 78% naphtha, 7% heavier and the balance gases and oxygenates. The high gasoline yield from this processing implies a high methane yield as well. This is apparently not a problem in South Africa which is short of natural gas. However, in most other places this would be a problem since natural gas is currently in over supply.

South Africa operates its F-T plants to make fuel, but also sells specialty chemicals after separating them from the diverse F-T product. For instance, they sell wax and purified oxygenates. Total product sales coupled with very low priced coal and essentially paid off plants allow them to break even against petroleum at a fairly low price. However, even they admit that they do not break even when petroleum is below about twenty dollars a barrel. Furthermore, some of the markets they sell F-T products into are nearly saturated even with the relatively small amount of product produced in South Africa.

Koebel's LPFT work continued for a while after the Second World War.⁹¹ The plant he and co-workers used contained a 1.55 meter diameter by 8.6 meters tall bubble reactor with internal cooling coils. The slurry of wax and catalyst moved upflow with co-current synthesis gas which contained hydrogen and carbon monoxide in the molar ratio of 0.7. The gas bubbles cause ebullition of the catalyst particles resulting in a well-mixed slurry. There was a recycle loop which allowed removal of wax product and spent catalyst. Fresh catalyst was also added on this loop to maintain catalyst loading at 10-20 wt% of the slurry. At a feed gas linear velocity of 9.5 cm/sec and operating conditions of 268° C and 12 atm. Koebel reported a temperature gradient of only 1° C and a catalyst concentration gradient of 0.2 to 0.6 wt% at 10 wt% average catalyst loading. Carbon monoxide conversion was 91% with 34.5 wt% of the hydrocarbon product in the range C_1 --- C_4 .

Koebel reported conditions for operating the slurry bubble reactor which produced extraordinary hydrocarbon distributions. For instance, with 50-500 g of catalyst per liter of suspension, catalyst particle size of 0.002--> 1 μ m, gas flow rate 10-30 times the percent weight of catalyst base metal in the suspension (gas flow expressed as NL/hr/liter of catalyst suspension) and plant operating pressures of 3-150 atmospheres, he reported no methane in the product!⁹² However, in the review

of LPFT which he wrote with Ralek⁹¹ he says about 4% of the total product from the 1952-1953 demonstration plant campaign was methane + ethane. Even this is quite low, particularly in light of the fact that the plant was being operated under conditions favoring production of gasoline not diesel fuel, and the carbon monoxide conversion was 90%. High conversions favor high methane + ethane selectivity.

LPFT research was continued in the U.S. after the Second World War by the U. S. Bureau of Mines.⁹³ After the Bureau of Mines work until the early 1980's additional liquid phase processing research was continued at various laboratories; a review was published in 1983.⁹⁴ Liquid phase processing was aggressively pursued in the 1980's, for instance, Mobil finished an LPFT contract in 1985.⁹⁵ Performance results from this and Koebel's earlier work are compared in Figure 3.

Currently research and development on liquid phase reactors and F-T catalysts to use in them is being done in many laboratories. The hydrodynamics of such reactors as well as kinetic rates of the various processes which have been performed in them have been studied and summarized by Deckwer⁹⁶ and Fan.⁹⁷⁻¹⁰⁰ Catalyst development is currently being sponsored by the DOE at the University of Kentucky and Texas A & M University.

The DOE is also sponsoring an international consortium of private companies for operation of a 0.572 m diameter slurry bubble reactor at LaPorte, Texas. One of the consortium members, Air Products and Chemicals, Inc. (APCI) provides site support. An LPFT reactor of this type is purported to be operational in South Africa, possibly about 1 meter in diameter. In addition, Exxon, Statoil and RENTECH have respectable internal projects for LPFT development. RENTECH have constructed a plant near Denver, Colorado to convert synthesis gas from biogenetic

methane formed at a waste disposal site. Finally, APCI have made a major effort to commercialize the slurry bubble concept for alcohol synthesis before their involvement in the DOE LaPorte consortium.

A slurry autoclave reactor (stirred tank) is usually used to screen LPFT catalysts; it was the only reactor used during this contract. In one case a catalyst was evaluated which later was used in a run at the LaPorte facility. Although this catalyst was not prepared as part of this contract its slurry autoclave pilot plant performance results are included to allow comparison to the performance in the LaPorte test. APCI is separately reporting the LaPorte test which took place in 1992. Some additional catalyst evaluation work was done at UOP in support of the LaPorte testing; these tests are included in Attachment 1. The catalyst performance targets of this contract are for use in a LaPorte type reactor. To estimate such performance from slurry autoclave pilot plant results additional crossover experiments are needed. From such experiments a mathematical model can eventually be derived, possibly based on several slurry autoclave reactors operating in series.

One problem contemplated with LPFT processing is separation of the catalyst from the liquid phase. This is necessitated because the F-T product can contain non-distillable (wax) reaction products. Probably the easiest way to minimize this problem would be to use a catalyst with an α which favors high light ends selectivities (low wax). However, this is a limited solution since a low wax catalyst invariably is excessively selective to methane and ethane. Furthermore, LPFT kinetics favor double α behavior which insures some wax product even from high light end's selective catalysts. In turn, this means catalyst/wax separation will always be necessary. The Mobil work of the mid-1980's showed that a relatively iron-free wax could be produced by known solid-liquid separation

technology. However, the wax still contained several hundred parts per million of iron and even this is sufficient to require a separate iron removal step to protect, for instance, the hydrocracking catalyst used to crack the wax to diesel boiling range material.

Catalyst particle integrity in the F-T reactor is important for LPFT. Particle attrition will magnify the separation problem. However, determining catalyst particle stability is a difficult experimental problem. Determining particle/particle attrition alone might not be enough. Particles could also attrit due to build up of stress from pressure within catalyst pores resulting from formation of long carbon chains. This would be similar to the spalling that the chromium on silica polyethylene catalyst is known to undergo. Direct measure of the rate of attrition of the catalyst particles in the stirred autoclave might also prove erroneous since the particle/particle attrition might be far different than in the slurry bubble reactor. Therefore, catalyst particle integrity data from a slurry bubble reactor will eventually be needed. Only a limited amount of work was done during this contract as a start toward understanding particle integrity.

3. EXPERIMENTAL SUMMARY

This section summarizes all of the experimental work done during this contract. Partial summaries of this work appear in the thirteen previous quarterly reports.

3.1 CONTRACT TASK 1.2. PRECIPITATED CATALYST PREPARATION

METHOD DEVELOPMENT

3.1.1 INTRODUCTION

Section 3.1.2 describes the catalyst preparation method, including the pilot plant used to prepare iron/copper oxide and iron/copper/silicon oxide catalyst precursors, and the subsequent steps to furnish a properly-sized, potassium-containing oxide.

3.1.2 CATALYST PREPARATION METHOD

Catalysts were prepared by precipitation. Drawings of the precipitation plant and an enlargement of the precipitation reactor are in Figures 4 and 5 respectively. Photographs of the plant are in Figure 6. A small, but high throughput, reactor was used to mix two aqueous solutions, one containing iron and copper nitrates and the other either sodium carbonate or sodium carbonate and sodium silicate. The driving force for the precipitation was the pH change due to sodium carbonate.

In addition, water was added at two places near the bottom of the reactor to facilitate removal of precipitate.

Two pH probes were provided, one in and one below the reactor. The initial plan was to control the amount and quality of the precipitate by maintaining constant pH by frequent changes in the feed rates. Most of the precipitation runs were performed this way. Feedback control of this nature did not work because the rate of the feedback control loop was too long compared to the run length. Runs had to be short since the feed rates were very high, even though the reactor was small, resulting in a large mass of precipitate going to a very slow filtration unit. This unit consisted of a bag filter with means to collect and recycle overflow liquors. Typically about one half of the precipitate was collected on the bags during and just after the run and the remaining one half on the next day when all of the overflow liquors were filtered.

In the final mode of plant operation the feed rates were adjusted to levels known to produce near quantitative precipitation of iron, these rates were maintained during the run. Runs 30, 32 and 33 were the final runs performed during this contract and all were performed with constant feed rates. Previous runs provided material suitable for catalyst preparation even though they were not performed under conditions which allowed consistently high yields of precipitate. Figure 7 briefly outlines the conditions used for these three runs. The rate of formation of precipitate on a dry basis was 500 g/hr. Sodium silicate was only added to the sodium carbonate solution during Run 33. Plots of actual feed rates and pH's vs. time on stream for Runs 32 and 33 are in Figures 8 and 9. Throughout both runs the actual feed rates were quite steady. The reactor pH was lower and less constant than the outlet pH. The reactor pH in both runs was quite low at the beginning, perhaps

due to a line out problem with the pH meter. The outlet pH was about 5.5 in both Runs 32 & 33.

Mass balance data for Runs 30, 32 and 33 are in Figure 10. The "direct filtered" and "overflow filtered" solids are separately reported. The total weight of iron and copper recovered increased over the three runs as the operators gained experience running the plant. Large losses can result from spills and overflows during filtration. Only small amounts of iron and copper but possibly larger amounts of silicon were lost due to solubility in the aqueous liquors. The low solubility of iron and copper are obvious from the experiment outlined in Figure 11 which reveals that 3 and 4 wt ppm, respectively, of iron and copper are soluble. These concentrations amount to losses of 0.05 wt% and 1.8 wt% of the iron and copper.

Figure 12 is the X-Ray diffraction pattern of the solid material removed as part of the experiment outlined in Figure 11. It reveals an amorphous iron oxide material, this is not surprising since the material was only dried, not calcined. As in other X-Ray spectra of materials made during this contract, the copper oxide pattern was missing. It is likely, therefore, that copper is well-dispersed throughout the iron oxide.

After sodium removal, the precipitates were further processed according to the scheme outlined in Figure 13. The final product was a material similar in size to the nominally 70 micron diameter commercial catalytic cracking catalyst. Cracking catalyst is a bound Y zeolite used for fluid catalytic cracking (not a liquid full reactor!), therefore, it is not clear whether the LPFT catalyst has to have exactly the same size. However, some lower limit on particle size will probably be needed since separation of catalyst from product wax must be done and particle size will affect the

ease of this separation.

Losses were taken at each step in Figure 13, those from Runs 30, 32 and 33 are summarized in Figure 14. The overall recoveries in Runs 32 and 33 were about 53% based on the amounts of iron, copper and silicon fed to the precipitation reactor. A major loss occurred during the final sizing to 140-400 mesh particles. Commercially, means would probably have to be found to recycle the through 400 mesh particles which account for the losses during sizing.

Potassium is the historic metal of choice to control activity and alpha in F-T processing. It was used in all of the catalysts of this work with the exception of one catalyst prepared during the study of the affect of the activation procedure on catalyst performance. Several ways of adding potassium were used in this work. One method used was impregnation of potassium carbonate from an aqueous solution. This is also a common method used by other F-T experimenters.

Figure 15 is a tabular summary of the on filter and overflow oxide properties from Runs 30, 32 and 33 after the work-up outlined in Figure 13. The conditions during Runs 30 and 32 were the same, and the elemental analyses of the direct and overflow filtered materials were about the same. However, there were differences in the surface area and pore volumes, the Run 32 materials having higher surface areas and lower pore volumes. Samples from Runs 30 and 32 samples were also analyzed by STEM (scanning transmission electron microscopy). Photographs resulting from these analyses are reproduced in Figures 16 and 17. The Run 32 samples contained smaller crystallites than those from Run 30. This is consistent with the higher surface area observed for these samples. Oxide samples from Runs 30 and 32 were converted to F-T catalysts and their performance in a standard slurry autoclave test were determined (Section 3.5.4, this report).

3.2 CONTRACT TASK 1.3. NOVEL CATALYST PREPARATION METHODS INVESTIGATION

3.2.1 INTRODUCTION

Two novel catalyst types are discussed as well as development of a method to prepare oil-dropped iron oxide spheres. One of the two catalyst types resulted from use of organo-potassium compounds to replace potassium carbonate as a source of potassium activator. The second type resulted from direct formation of high surface area potassium/iron/copper and iron/copper carbides from the corresponding oxalates followed by addition of potassium from an organo-potassium compound. Pilot plant performance data for these catalysts are in Section 3.5. The sphere forming experiments involved hydrolysis and gelation of an organo-iron compound dissolved in bubbles of mineral spirits suspended in an essentially aqueous forming liquid.

3.2.2 USE OF ORGANO-POTASSIUM COMPOUNDS

Organo-potassium compounds are soluble in organic media such as the hot oil present during LPFT. It is, therefore, possible to add such compounds to the oil and iron/copper oxide before start up or as a solution during a run. The effect of these compounds on the catalyst performance is different than expected based on work during this contract with potassium carbonate activated catalysts. Specifically, catalysts resulted which were less selective to methane + ethane. Furthermore, organo-potassium compounds are easier to employ than potassium carbonate which requires aqueous impregnation/calcination.

Three different organo-potassium compounds were used: potassium laurate, potassium benzoate and potassium nonylphenolate. Potassium laurate was the most extensively studied of the three, and produced the low selectivities mentioned above.

In some runs potassium laurate was added to the reactor with the metal oxide and start up oil before the start of a run and in other cases it was added intermittently as a solution in isopropanol/heptane during a run. Potassium laurate was also used in combination with potassium carbonate impregnation. In this case it was added as a solution to a catalyst containing potassium from potassium carbonate impregnation.

Potassium laurate-derived catalysts were less active at a given potassium level than those from potassium carbonate. However, they continued to gain activity at high potassium levels which levels resulted in activity loss when potassium carbonate was used. Methane + ethane selectivity continued to decrease at high potassium levels regardless of the potassium source.

Potassium nonylphenolate was evaluated in just one run. It was added intermittently as a solution in isopropanol/heptane to a catalyst which contained some potassium from potassium carbonate. In this case the effects on conversions and methane + ethane selectivity were directionally the same as with potassium laurate. However, the amount of change in these two was much less per gram of potassium than with potassium laurate.

Potassium benzoate was also evaluated in one run. In this run potassium laurate was added to the iron oxide at start up to furnish the initial potassium. Later an isopropanol solution of potassium benzoate was added. Addition of potassium benzoate produced a slight increase in the carbon

dioxide selectivity but no change in conversions or light ends selectivities.

The actual tests of the organo-potassium-derived catalysts are outlined in Section 3.5 along with tabular comparisons to a potassium carbonate-derived reference catalyst.

Koebel in his seminal LPFT studies used organo-potassium compounds as well as inorganic ones.¹⁰¹

Claim 1 of the above referenced patent is to an improved process *"which comprises continuously passing a synthesis gas into a hydrocarbon oil product suspension of carbon monoxide hydrogenation catalyst having a concentration....."* Clearly this is a process description of LPFT.

A subsidiary claim of the Koebel patent describes the alkali component of the catalyst for this process: *"Improvement according to claim 9 in which said suspension within said reactor possesses a predetermined alkali content, and in which said alkali content is maintained substantially constant by adding together with said replacing oxidic compound a catalyst based percentage of alkali material higher than that of said predetermined alkali content."* Another subsidiary claim describes use of surface tension modifying agents; potassium stearate is a specific example given in the body of the patent.

Although Koebel describes the use of potassium stearate, and makes a comment in the body that the surface tension modifying agent might be one which increases or decreases the surface tension, he does not describe a special effect on conversion and/or selectivity. The use of an organo-potassium compound to facilitate low methane + ethane selectivity at high conversion seems unique to the current work. Furthermore, it has been found that all organo-potassium compounds do not behave in the same way when added to the catalyst system in solution during a run.

3.2.3 NOVEL METAL OXALATE-DERIVED CATALYSTS

Preparation of F-T catalysts via decomposition of metal complexes is known but has not been extensively developed^{63, 102-104}. However Soong, et. al.⁶³ did decompose $\text{MnFe}_2(\text{C}_2\text{O}_4)_3$ to form an iron/manganese F-T catalyst. This method was used during this contract to convert a mixture of potassium, copper and iron or copper and iron oxalates into high surface area mixtures of iron carbides by the steps below:

Heat, Vac

250-300° C, Atm. Pressure

65 psig, 250-300° C

The preparation above was accomplished in a modified Mettler TA-2 thermal analytical balance. This allowed careful measurement of the mass changes as the various steps of the synthesis were performed. The oxalate decomposition step was performed with pure hydrogen. To accomplish the third step the pressure was first raised to 65 psig with hydrogen, then the carbon monoxide was added to the gas flow. The change in mass indicated that carbides were formed within less than an hour. Thereafter, F-T activity was demonstrated by the accumulation of wax in the analytical balance, as witnessed by a weight gain and actual wax accumulations in the apparatus.

Furthermore, careful analysis of the gas exiting the analytical balance showed the presence of typical F-T product gases such as methane and ethane. Several such carbide preparations were performed and the products were allowed to operate as F-T catalysts in the thermal balance for extended periods of time. It was thus found that the oxalate-derived carbides were stable at 250° C during 100-120 hour runs with either 2 : 1 or 1 : 1 molar hydrogen : carbon monoxide. However, at 300° C the catalyst lost all activity after fifty hours. An X-Ray diffraction analysis of a wax/catalyst sample was removed from the analytical balance is attached as Figure 18. This analysis indicates the presence of Fe_5C_2 and $\text{Fe}_{2.5}\text{C}$ and possibly several others as well.

A report summarizing this work more fully is attached as Appendix 3. A large sample of a copper/iron carbide was prepared in a similar fashion and evaluated in the autoclave pilot plant with potassium added as potassium laurate; its performance is outlined in Section 3.5.

3.2.4 OIL-FORMED IRON OXIDE SPHERES FROM A SOL-GEL ROUTE

The sol-gel method of preparing iron oxide catalysts is a desirable approach for improving catalyst mechanical strength because this method allows formation of spheres which are the most attrition resistant shape for catalyst particles.

The preparation of binderless iron oxide spheres has been achieved by the development of a novel sol-gel forming procedure. The starting material is a solution of Fe(III) 2-ethylhexanoate in mineral spirits which is added dropwise to an ammoniacal solution of methanol. The low viscosity of the methanol causes the formation of small droplets of the iron solution. The immiscibility of the mineral spirit solution in the methanol, and the difference in surface tensions between the two

solutions, causes the droplets to assume a spherical shape. Low levels of ammonia and water in the methanol promote the hydrolysis of the Fe(III) 2-ethylhexanoate causing the spherical particles to gel (harden). The iron containing spheres can then be isolated by filtration. These are the first reported spheres of 100% iron oxide phase, prepared without a binder. Initial preparations have resulted in 100-200 μ diameter spheres.

Some as yet insurmountable mechanical difficulties were encountered in the scale-up of this new method. The principal problem results because the current method for introducing appropriate size liquid droplets of the Fe(III) 2-ethylhexanoate into the forming liquid is inadequate. This method does not control the associated formation of "powder" material, which consists of very tiny (1-10 μ), but spherical particles. Several alternate methods of addition were tried. These included several sizes of eye droppers and a variety of air brush fittings. The droplets formed using the eye droppers were too large to be supported by the low viscosity methanol and broke up into smaller droplets. This left a trail of the aforementioned powder. The air brush was used in an attempt to break up the solution into a finer stream of particles before entering the methanol solution. This method reduced the number of particles having a spherical shape, presumable due to loss of too much solvent from the Fe(III) 2-ethylhexanoate solution prior to contact with the ammoniacal methanol forming solution. It might be possible to overcome this problem by increasing the dilution of the Fe(III) 2-ethylhexanoate prior to passing it through the air brush assembly.

Optimization of the level of ammonia in the methanol solution depended on the size of the Fe(III) 2-ethylhexanoate droplets. A range of 2.5-->5.0 wt% aqueous ammonium hydroxide worked best when an eye dropper was used to form the droplets. The use of higher levels of ammonia with the eye dropper, did not permit the droplets to break up. This resulted in incomplete hydrolysis

throughout the, now very large, spheres. The introduction of smaller initial droplet sizes permits the use of a higher ammonia concentration and speeds up hydrolysis. An upper limit on the aqueous ammonia addition is reached when the density of the ammoniacal methanol becomes too high, relative to that of the mineral spirit solution of Fe(III) 2-ethylhexanoate, and the droplets no longer sink through the forming medium.

3.3 CONTRACT TASK 3.3. CATALYST ACTIVATION

3.3.1 INTRODUCTION

During use the iron-based F-T catalyst is known to consist of oxidic as well as carbidic iron. In addition, several iron carbides have been characterized in the working F-T catalyst. Therefore, it might be possible to alter the performance of the catalyst by changing the types and/or amounts of the various iron species present during operation. One way to do this might be by changing the composition of the catalyst through activation procedure changes. Two activation procedures have been used in this work. In the first the catalyst was pretreated with the 0.7 molar hydrogen : carbon monoxide ratio synthesis gas which was also the plant feed. In the second the catalyst was pretreated with carbon monoxide. The catalyst performance was affected by the activation procedure.

3.3.2 ACTIVATION WITH SYNTHESIS GAS

The feed gas in all of this work was a simulated coal-derived synthesis gas with a $H_2 : CO$ molar ratio of 0.7. In most of the catalyst evaluations during this contract the feed itself was used to activate the catalyst. Performance results with catalysts activated in this fashion are in Sections 3.5-->3.7. In these cases the pretreatment occurred after the iron/copper oxide and start up oil were loaded into the autoclave reactor. The activation procedure was fifteen hours long during which time the feed was processed at $2.0 \text{ NL/hr} \cdot \text{g Fe}$ and the reactor was maintained at 280° C and 153 psig. After this the normal processing conditions of $2.4 \text{ NL/hr} \cdot \text{g Fe}$, 265° C and 290 psig were established. During and after catalyst activation the stir rate was 1100 RPM. When activated in this fashion the iron/copper oxides prepared during this work produced catalysts that were moderately active and exhibited low methane + ethane selectivity. Carbon monoxide conversions with some of the better catalysts were about 70% at line out. Since the objective of this contract is a low methane + ethane catalyst, this activation procedure was used while other aspects of the catalyst which might give improved conversion and/or even lower methane + ethane selectivity were evaluated. For instance, this activation procedure was used with a series of catalysts which were similar in all regards except in the level of potassium promoter (Section 3.5.6 below). Of all the catalysts so-activated in this work, including a reference catalyst from Ruhr Chemie, the best one from the standpoint both of high conversion and low methane + ethane selectivity was the one resulting from a novel addition method of the potassium promoter. This catalyst was evaluated in Run 49 which is described in Section 3.5.7 (particularly see Figure 19). With this catalyst the carbon monoxide conversion at the standard conditions was 70% and the methane + ethane selectivity was 3.4 mole%.

3.3.3 ACTIVATION WITH CARBON MONOXIDE

Two runs were performed with catalysts resulting from carbon monoxide activation; catalyst performance results are reviewed in Section 3.5.11. In both runs the same iron/copper/silicon oxide catalyst precursor was used, the properties of which are in Figure 20. In the first run potassium was added to the catalyst composition at start up and in the second run it was added during the run. Both times the source of potassium was potassium laurate which has proven during this contract to be a way of transferring potassium to the catalyst (Section 3.5.7).

In the first run 72.7 g of iron/copper/silicon oxide along with 6.7 g of potassium laurate and 290 g of C₃₀ oil were loaded into the autoclave reactor. The calculated potassium : iron weight ratio was 2.4 : 100. A carbon monoxide flow was established after the metal oxide and start up oil were added to the autoclave reactor. The activation took twenty-six hours. However, the carbon monoxide was fed to the reactor beginning at room temperature whereas in the shorter synthesis gas activations above the reactor was brought to the activation temperature under nitrogen prior to starting the synthesis gas. The reactor temperature and pressure during activation were the same as during the subsequent run, namely 265° C and 200 psig.

During activation carbon dioxide was produced by reaction of carbon monoxide with the metal oxide catalyst precursor and possibly by the Boudouard reaction as well:

If too much carbon is formed from the Boudouard reaction, catalyst deactivation could result,

therefore, excessive activation times were avoided.

Product gas analyses during the first run's activation period are summarized in Figure 21. The amount of carbon dioxide increased as the temperature increased, but then declined shortly after the target temperature was reached, probably due to near full reduction of the iron oxide to iron carbides. A small amount of carbon dioxide was noted, however, even at the end of the activation period, possibly from the Boudouard reaction.

The second carbon monoxide activation run employed 290 g of C₃₀ start up oil and a fresh 72.3 g sample of the same iron/copper/silicon oxide used in the first run. This time no potassium laurate was added at start up, but it was added as a solution in isopropanol/heptane during the run. The activation procedure was the same used in the first run; product gas analyses during the activation are summarized in Figure 22. The amount of carbon dioxide formed and the rate at which it was formed were approximately the same as in the first carbon monoxide activation run.

Independent work by Burt Davis and co-workers at the University of Kentucky as part of their current Fischer-Tropsch contract has shown that no iron oxide is left after an activation of this type. However, they find that some iron oxide is reformed during F-T synthesis. Therefore, from the standpoint of the gross structure of the operating catalyst, there do seem to be similarities regardless of the mode of activation. However, the two activation procedures do not produce catalysts which exhibit similar performance. During this work and that at the University of Kentucky more active catalysts have resulted from carbon monoxide activation than synthesis gas activation. However, carbon monoxide activation has also resulted in high methane + ethane selectivities. This selectivity resulted in part because the catalysts were so active (light ends selectivities increase at high

conversions). However, since the selectivity could not be effectively controlled by potassium the carbon monoxide method of catalyst activation was not pursued beyond these two runs.

3.4 CONTRACT TASK 1.5. CATALYST CHARACTERIZATION

3.4.1 INTRODUCTION

Various techniques were used to characterize fresh oxide catalyst precursors and used catalysts including scanning transmission electron microscopy (STEM), Moessbauer, X-Ray diffraction, magnetic measurements, nitrogen porosimetry and elemental analysis. Section 3.4.2 outlines experiments done with catalysts withdrawn at various times during a fifty hour run. Section 3.4.3 covers work performed to find a way to determine differences in fresh oxide mechanical strength.

3.4.2 CHARACTERIZATION OF CATALYSTS WITHDRAWN DURING FIFTY HOUR RUN

Samples of catalyst suspended in wax were withdrawn at 4, 12, 24 and 50 hours during Run 32 (a 50 hour run). These samples were analyzed by Moessbauer, X-Ray diffraction and magnetic susceptibility. The results of these tests are summarized in Figures 23-27. The Moessbauer data show the rapid conversion of Fe_2O_3 to Fe_3O_4 and a slower conversion to carbidic iron species. These changes began during the catalyst activation period and continued thereafter. These results

correlate well with the X-Ray and magnetic measurements.

The X-Ray data show, in addition, that the original Fe_2O_3 had crystallites on the order of 10 nm whereas the Fe_3O_4 had crystallites of 15-25 nm.

The magnetic susceptibility data suggests that the iron carbide is accompanied by a more complex type magnetic material which could be a mixture of iron carbides and oxides. Continued reduction in magnetism as the run progressed could be indicative of formation of more highly carbonized material.

The fifty hour run was one of four, each with a fresh sample of the same catalyst. These runs demonstrated that the slurry autoclave plant could be operated in a reproducible fashion. Performance results from these runs in Section 3.5.5 illustrate that the selectivity to light products such as methane and ethane increased during the activation period. This increase continued after the activation period but at a decreasing rate. The conversions, on the other hand, increased during activation then decreased as the runs progressed. The selectivity changes thus do not seem to be tied just to conversion. The increase in light product selectivities during the early stages of a run probably are due instead to changes in the nature of the catalyst. Although these changes are complex, it is tempting to speculate that more highly oxidized catalyst is less selective to light products. If this is the case, ways might be discovered to maintain the catalyst in a more highly oxidized state during a run wherein low light product selectivity is desired.

3.4.3 SILICON VS. SILICON-FREE OXIDES: MECHANICAL STRENGTH

Oxides from precipitation plant Runs 32 (no silicon) and 33 (1.25 wt% silicon) were compared with respect to mechanical strength. Aqueous slurries of the two samples each with mean particle diameter slightly less than 100 μm were subjected to sonic mixing. Particle size measurements were made by a laser light scattering method at 0, 2, 5, and 10 minutes. The results summarized in Figure 28 show that the silicon-containing oxide was mechanically stronger.

3.5 CONTRACT TASK 2.0. CATALYST TESTING

3.5.1 INTRODUCTION

Section 3.5.2 describes the method of testing the catalysts including the slurry autoclave plant used for the catalyst evaluations, and the standard catalyst activation procedure. The initial runs were performed with a reference catalyst prepared during this work, and are outlined in Section 3.5.3. These runs demonstrated the reproducibility of the slurry autoclave catalyst evaluation test; during one of them catalyst samples were withdrawn intermittently between startup and fifty hours on stream to determine changes in the catalyst properties as a function of time on stream. Analyses of these withdrawn catalyst samples are reported in Section 3.4, Catalyst Characterization. Evaluation of a reference (formerly commercial) catalyst from Ruhr Chemie is outlined in Section 3.5.4. Two identical precipitation plant runs from near the end of this work provided iron/copper oxides for the pilot plant runs outlined in Section 3.5.5. When these oxides were prepared the run to run

oxide yield was high, but there were still some changes in the physical properties of the precipitates (Section 3.1). Section 3.5.6 describes evaluation of catalysts from the same lot of oxide precipitate, but with varying levels of potassium from potassium carbonate impregnation. An alternate and less time-consuming method of potassium addition was used to prepare the catalysts outlined in Section 3.5.7. Runs with additional catalysts prepared using a similar potassium addition method are reviewed in Section 3.5.8. In Section 3.5.9 two catalysts from the same precipitation run, but differing in mesh size are evaluated. The performance of the novel metal oxalate-derived catalyst is outlined in Section 3.5.10. Catalyst performance after activation with carbon monoxide is described in Section 3.5.11. Evaluation of an aliquot of the catalyst manufactured by United Catalyst Inc. and evaluated at the LaPorte, Texas slurry bubble reactor is outlined in Section 3.5.12.

3.5.2 THE CATALYST TESTING PROCEDURE

Since pilot plant-scale slurry bubble reactors are not readily available it has been the custom to screen LPFT catalysts in slurry autoclave reactors. A diagram of the slurry autoclave plant used during this contract is in Figure 29. The reactor was contained in an insulated "hot box" maintained at 130° C. Additional heat was supplied to the reactor to achieve the operational temperature which was usually 265° C, although slightly higher temperatures were sometimes desired. Figure 30 contains a sketch of the part of the plant contained in the hot box, whereas Figure 31 contains a detailed drawing of the autoclave reactor itself. The F-T reactions are very exothermic, the liquid was, therefore, hotter than the gas this allowed the liquid level to be determined from temperature measurements up and down the thermowell shown in Figure 31.

F-T catalysts are easily deactivated by feed impurities, particularly sulfur. For this reason pure carbon monoxide : hydrogen blends were purchased from Scott Specialty Gases, Troy Michigan. Furthermore the autoclave plant contained a feed pretreatment section consisting of 1265 cc of alumina spheres maintained at 210° C and 515 cc of 13X molecular sieves maintained at room temperature. The alumina and molecular sieves were replaced by fresh material twice a year.

Means were provided to remove gas and liquid from the autoclave. In both cases removal was through cylindrical stainless steel filters (shown shaded in Figure 31). These filters were 1 1/2 in. long, by 3/8 in. outside diameter (1/4 in. inside diameter), they removed all but the finest catalyst particles. The filters plugged periodically, a positive pressure of feed usually served to unplug them, however, when this failed redundant filters were available. The redundant wax filter is shown in Figure 31. An unfiltered gas outlet was also available for emergency venting. Some catalyst fines were usually observed in withdrawn liquid (wax) from the first few periods of the run. After that, however, the wax contained very little catalyst by sight or analysis.

The F-T products were collected as both gases and liquids. Two of the traps used to collect liquids were in the hot box. (Although only two are shown each had a backup as did the traps outside of the hot box. This allowed one set of traps to be emptied while the second set was collecting products.) One hot box trap contained condensate from the continuous removal of autoclave overhead gas. The other contained the wax resulting from intermittent removal of a part of the autoclave liquid phase which was done often enough to maintain the liquid level 6.5 ± 1 inches from the bottom of the autoclave. This material usually was a solid after the trap was removed from the hot box and cooled to room temperature.

There was a second set of three traps outside of the hot box. The first was maintained at 0° C and the second and third at -70° C. It was found during this work that the third trap was needed to collect material that would not condense in the first two.

Two on line gas chromatographs analyzed slip streams of the hot box effluent. The first one (GC-1) performed a boiling point analysis for molecules with as many as 20 carbon atoms. The sampling valve for this chromatograph was before the first of the three traps exterior to the hot box. Unfortunately the concentrations reported by this instrument were erroneous. This was the case even after attempts to adequately heat the line and sampling valve. Heavy molecules appeared to condense into the line and/or valve during the time between samplings resulting in injection of a heavies-rich sample into the GC. The sampling valve for the second GC (GC-2) was between the first and second exterior trap. This GC performed a gas analysis and worked well. For purposes of mass balancing the plant and calculating Schulz-Flory data, this GC was used to obtain the weights of C₁-C₄ hydrocarbons. The amounts of these hydrocarbons in the first external trap were added to the GC-2 amounts, but this was a small correction. Oxygenates are not available from GC-2, in cases where selectivities to these products are reported GC-1 data were used. Most of the oxygenates were alcohols, aldehydes were found but in low levels.

The products collected in the traps were sometimes submitted for off line analyses. In cases where a Schulz-Flory plot was desired this had to be done. The sample from the hot box trap which resulted from autoclave liquid withdrawals was analyzed by liquid phase chromatography. This sample was usually a solid wax. The other hot box sample and the hydrocarbon samples in the external traps were analyzed by a boiling point gas chromatographic method. The aqueous products, which were found only in the traps external to the hot box, were analyzed for organic

molecules by gas chromatography. A complete breakdown of the products by carbon number was obtained by these off line analyses combined with the on line gas analysis for C_1 - C_4 hydrocarbons

Conversions and selectivities were calculated with the aid of an argon internal standard in the 0.7 molar H_2 : CO feed. Selectivities reported are on a carbon dioxide-free basis. In other words, since about one half of the carbon monoxide was converted to carbon dioxide, the reported hydrocarbon selectivities are about twice what they would be if carbon dioxide selectivity were taken into account in their calculation.

In this work 72.7 g of oxide were usually used, however, in some cases 25 g were used. The high oxide amount provides 20 wt% solids in the slurry which is the target of this contract. The lower solids level was originally used for catalysts which were in short supply, however, reference runs at this loading were also performed. In all cases 290 g of a product from the Ethyl Corp. was loaded with the oxide. It is called Ethylflo 30 and is essentially a C_{30} oil. In most cases this worked well as a start up oil to be replaced during a run by product wax. The exception occurring during evaluation of catalysts which produced low levels of wax, in such cases the C_{30} oil exited with the autoclave vapors faster than it could be replaced by heavy reaction products.

High loading of catalyst into the slurry oil will be a key to the success of LPFT processing. At 72.7 g of oxide and 290 g of oil a 20 wt% loading is attained. This is now considered to be a high enough loading to be a target for this contract.

3.5.3 CERTIFICATION OF THE SLURRY AUTOCLAVE TESTING

PROCEDURE

Four runs were performed with separate fresh samples of the same oxide to evaluate run to run reproducibility of the autoclave plant. Properties of this oxide are summarized in Figure 32. One of these was a short run (50 hours) from which catalyst samples were periodically withdrawn for characterization, the results of which are summarized in Section 3.4 of this report.

The activation procedure for the four reproducibility runs was the one used subsequently for most of the other runs during this work. It consisted of a fifteen hour pretreatment with the synthesis gas feed at 2.0 NL/hr · g Fe, 280° C, and 153 psig plant pressure. The stir rate before and after pretreatment was 1100 rpm. After pretreatment the operating conditions were: 2.4 NL/hr · g Fe, 265° C and 290 psig.

Performance data for the three longer runs are compared in Figures 33-39. The conversions, light product selectivities and H₂/CO usage were all closely reproduced in each run. The data for the short run were also virtually superimposable on that from the first fifty hours of the three longer runs. One reason for this was the extreme care taken to control the temperature (Figure 33).

The conversions followed a pattern observed for many iron catalysts in this work: a rapid conversion increase during the activation period followed by a line out period during which the conversions (and selectivities) were changing—in this case the conversions decreased and the light hydrocarbon selectivities increased. These changes were still taking place at the ends of the runs albeit at ever slower rates.

The selectivities changed due to the catalyst aging process, not due to the change in conversion. For instance, it will be shown below that the conversion/selectivity relation on a similar, but lined out, catalyst was just the opposite to that above—lower conversions in that case resulted in lower methane selectivities. Conversion changes with the lined out catalyst resulted from feed rate changes. It is possible that operating conditions can be found to maintain the low methane + ethane selective iron phase(s) present during the early part of a run. This has not been done during the current work.

3.5.4 EVALUATION OF REFERENCE RUHR CHEMIE CATALYST

Ruhr used to furnish commercial quantities of an oxidic F-T catalyst precursor. Although no longer available in large quantities, small samples are available for use as a reference. The properties of this material as measured at UOP are in Figure 40. It was evaluated in the slurry autoclave plant under the conditions used for most of the tests in this contract (Figure 41). The conversions from this catalyst were not extraordinary compared to the catalysts developed during this contract (Figure 42). The selectivities to light products were high compared to the objectives of this contract and to catalysts developed under it (Figures 43-47). For instance, at the end of the 250 hour run when the catalyst appeared to be nearly lined out the methane + ethane selectivity was 7.7 mole % (72% CO conversion).

3.5.5 COMPARISON OF CATALYSTS FROM IDENTICAL PRECIPITATION RUNS

Four catalysts were evaluated, two each from precipitation Runs 30 and 32 oxides (one direct and

one overflow filtered sample per run). In these runs 25 g of iron/copper oxide were used, with 290 g of oil. Potassium was added as solid potassium laurate along with the oxide and oil. Enough potassium laurate was used so that the iron : potassium wt. ratio was 100 : 1.8. The 0.7 molar $H_2:CO$ feed was used. The operating conditions before and after the activation were the same as outlined in Section 3.5.2 except the feed rates were 5.8 and 7.0 NL/hr $\cdot$ g Fe respectively. Because of the higher feed space velocity the conversions during these runs were lower than usual. Furthermore, the percent loss of conversion during line out was high (Figure 48). This was probably due to the first order nature of the conversion; a similar loss of activity can cause a greater or lesser loss in conversion depending upon whether the initial conversion was in the relatively flat or more steeply inflected part of the conversion/contact time plot.

A tabular summary of line out conversions and selectivities is in Figure 49. The catalysts from precipitation plant Run 30 were less active than the ones from Run 32. In both cases the overflow material produced a more active catalyst. Although the difference in conversion between the best and worst catalyst was high, even the Run 30 overflow catalyst exhibited the high conversion expected from work with other catalysts in this contract at the target feed rate of 2.4 NL/hr $\cdot$ Fe (obtained by reducing the feed rate-see Figure 48).

3.5.6 COMPARISON OF CATALYSTS FROM THE SAME OXIDE BUT WITH DIFFERENT LEVELS OF POTASSIUM

Five catalysts were evaluated, each from the same oxide but with different levels of potassium from potassium carbonate impregnation/calcination. The properties of the potassium-free oxide and the

potassium-containing oxides are in Figure 50. The catalysts were evaluated under the conditions used for plant certification (Subsection 3.5.3). As in previous runs catalyst activities and selectivities changed during activation and thereafter, but apparent line out performance was eventually attained.

Carbon monoxide conversions and methane + ethane selectivities at line out are summarized in Figure 51. A plot of carbon monoxide + hydrogen conversion vs. potassium level is in Figure 52. Catalyst activity dropped for potassium levels just above 2 g/100 g Fe. Methane + ethane selectivities dropped continuously as the potassium level increased (see also Figure 53).

Olefin to paraffin ratios at 73% conversion are summarized in Figure 46 ($C_2 \rightarrow C_4$). A space velocity reduction was made during the run with the low activity 2.7 g K/100 g Fe catalyst so that the conversion would be the same as with lower potassium catalysts.

Carbon dioxide selectivities were always high, even for the lower activity catalyst of Run 39 (Figure 55). Alcohol selectivities ($C_1 \rightarrow C_4$) are summarized in Figure 56, there was little difference as the amount of potassium changed. The sum of the alcohol selectivities varied from 2.5-->3.2 mole %.

The 2.06 g K/100 g Fe catalyst (Run 37) was the best of the five from the standpoint of high activity and low methane + ethane selectivity.

Product analyses of all trap products from three Run 37 periods were performed in order to determine the complete product distributions. The heavy product present in the hot box traps was analyzed by gel phase chromatography with a correction to account for any residual (start up) C_{30}

oil. The liquids in the traps outside the hot box (aqueous and hydrocarbon) were analyzed by gas chromatography. The on line gas analyzer (GC) data were used for C_1 -> C_4 hydrocarbons. Because some C_5 's and C_6 's were lost during trapping/transferring, the on line boiling point GC data were used to estimate the actual C_5 and C_6 yields. Schulz-Flory plots were constructed. The low carbon number end of these plots are in Figure 57; Figure 58 contains the full-range plots. The plots are of the so-called double-alpha type. A non linear regression method similar to that of Satterfield, was used to calculate $\alpha_1 = 0.67$ and $\alpha_2 = 0.92$ (all three plots). According to Satterfield his non-linear regression α 's are within 10% of the comparable linear regression α 's.

The total product analyses were also used to calculate the product distribution in each of the historic fuel ranges (Figure 59). As the catalyst approached line out less gasoline and diesel, but more heavies (C_{20+}) were produced.

3.5.7 EVALUATION OF POTASSIUM LAURATE-PROMOTED CATALYSTS

Potassium laurate is a readily available organo-potassium salt which, because of its surfactant nature, enjoys solubility in organic solvents. The original idea was that potassium laurate added at the start of the run would solubilize into the hot C_{30} oil and activate the oxide. This would eliminate two steps of the previous catalyst preparation, namely aqueous impregnation of potassium carbonate followed by calcination. The patent of Koebel suggested this might work.¹⁰³ As outlined below, it is possible to utilize potassium laurate in this fashion.

In the first run with it, 10 g of solid potassium laurate was added to 72.7 g of iron/copper oxide

(properties in Figure 60) and 290 g of C_{30} oil, the calculated Fe : K weight ratio was 100 : 3.2. The activation and post activation conditions were the same used in the autoclave plant certification runs (Section 3.5.3), the catalyst conversion performance is outlined in Figure 61. The conversion was not as high as that of the best potassium carbonate-derived catalyst, however, when the conversion was increased by reducing the feed rate a very low methane + ethane selectivity resulted (3.2 mole % at 70% CO conversion, see Figures 62 and 63). Plots of C_3 and C_4 hydrocarbon and light alcohol selectivities vs. hours on stream are in figures 64 and 65.

Schulz-Flory plots were made from three periods of this run. The results are summarized in Figures 66 to 68 as the C_1 -- C_{19} part of the Schulz-Flory curves. These plots contain raw data as well as the data resulting from the non linear regression analyses. The reported values for α_1 and α_2 , Xi and Phi are from the non linear regression analyses. Xi is roughly equivalent to the intersection of the two "straight lines" defined by the legs of the parabolic Schulz-Flory curve. The experimental values for C_5 and C_6 tend to be low when estimated by the on line GC analysis.

A relatively high level of potassium laurate was used in the first run due to concern that some would remain in solution and be lost during the periodic withdrawals of wax from the plant. However, this was not the case, the amount of potassium removed was very close to the amount one would predict based on the small amount of iron/copper oxide (fines) known to be present in the withdrawn wax. Figure 69 is a tabular summary of the iron and potassium levels in the product wax. Thus nearly all of the potassium laurate must have "found" the catalyst, resulting in a lower activity catalyst exactly as was the case when a similar (high) potassium level was present from impregnation/calcination of potassium carbonate.

In the following two runs a solution of potassium laurate in isopropanol/heptane (50 : 50 by weight) was added after the activation period. During these runs evidence was gathered indicating that potassium laurate promotion could lead to catalysts with lower methane + ethane selectivities. In the first of the two runs potassium laurate was added to a potassium-free catalyst, and in the second it was added to a catalyst containing a low level of potassium from potassium carbonate impregnation. The properties of the two iron/copper oxide precursors are in Figure 60.

In the first run intermittent addition of the potassium laurate solution began at 175 hours on stream (Figure 98). The result was an immediate increase in the carbon dioxide selectivity indicating an increase in the catalyst's ability to oxidize carbon monoxide to carbon dioxide. Somewhat later the Fischer-Tropsch activity of the catalyst increased as well with a concomitant reduction of the light ends selectivities (Figures 99 to 104).

The F-T activity continued to increase for potassium levels up to 2.5 g potassium/100 g iron. Thereafter, until potassium addition was terminated at 3.7 g/100 g iron there were further increases in either the carbon monoxide or hydrogen conversion. The H_2/CO usage ratio also decreased until the 2.5 g of potassium level was attained, but not thereafter. The carbon dioxide selectivity reached its maximum value at this potassium level. The changes in carbon monoxide conversion and methane, ethane and carbon dioxide selectivities as a function of potassium level are summarized in Figure 105. The immediate response of the carbon dioxide selectivity to potassium addition compared to the retarded response of carbon monoxide conversion and methane and ethane selectivities might mean that the active sites for carbon monoxide oxidation and reduction are fundamentally different, with the reduction sites requiring more than one potassium. If there is more than one F-T site the more active ones might require multiple potassium atoms. Multiple

potassium sites would accumulate more slowly than one potassium sites during the initial phase of potassium addition. If multiple potassium sites are more active for the F-T reactions, they might also be intrinsically less selective for light hydrocarbons since as the catalyst activates through addition of potassium these selectivities decrease.

The maximum conversions at the 2.5 g potassium level were less than either of the 2.1 g potassium catalysts previously described: potassium carbonate impregnated and solid potassium laurate at startup. For instance, the carbon monoxide conversion was 42% compared to about 70% for the two 2.1 g potassium catalysts.

Near the end of the run the operational temperature was increased in stages to obtain selectivities at higher conversions. Space velocity changes would probably have been a better way to achieve higher conversions since the catalyst is expected to be intrinsically more selective to light products at higher temperatures. However, the $C_1 + C_2$ selectivity at 290° C and 68% carbon monoxide conversion was only 3.4 mole%! This is a very low selectivity at this conversion even at 265° C.

In the second run the potassium laurate solution was added to a catalyst which had 1.0 g of potassium carbonate-derived potassium/100 g of iron on it at startup. This catalyst was initially more active than the one used in the previous run (Figure 106). For instance, the carbon monoxide conversion was 40% at seventy hours on stream just before potassium laurate addition began at seventy-five hours on stream. This addition was again intermittent. As in the previous run potassium laurate produced an immediate increase in the carbon dioxide selectivity (Figure 106). Activity gains were noted until the addition of enough potassium laurate to bring the total amount of potassium up to 2.0 g/100 g of iron. Further potassium laurate additions produced no activity

The second potassium laurate run was identical to the first except 6.5 g of potassium laurate was used (Fe : K wt. ratio = 100 : 2.1). A catalyst resulted which was close in activity to the 100 : 2.1 catalyst (Section 3.5.6) from potassium carbonate (Figures 70 and 71). From (90-140 hours on stream the wrong feed was used, however, after reintroduction of the right one the conversions returned to values similar to what they had been before. At 150 hours on stream the catalyst appeared to be lined out and condition changes were made to determine the affect of contact time on conversions and selectivities (Figures 72 to 75). At the end of the run the original plant operating conditions were re-established; at this time the conversions and selectivities were close to what they were at 150 hours on stream. At this time the carbon monoxide conversion was 73% and the methane + ethane selectivity was 5.2 mole %.

Samples of the wax withdrawn during the first three periods were again analyzed for iron and potassium. The amount of potassium was again about what one would expect based on the assumption that all of the potassium laurate had "found" the iron and was being removed as part of the trace amount of iron catalyst fines known to pass through the wax filter system during the early stages of a run.

Selectivity/conversion plots for methane and ethane are in Figures 76 and 77. These clearly show that a problem in achieving the target low $C_1 + C_2$ selectivity at high conversion is the rapid increase in this selectivity at high conversion. The H_2 to CO usage is less than 0.7 (Figure 78, the shape of this plot is typical for all iron catalysts operated at less than $280^\circ C$.¹⁰), but increases to approach 0.7 at high conversions. The result is that at high conversions the H_2 to CO usage increases this, in turn, can favor formation of high hydrogen products such as methane and ethane are favored.

Contact time/yield plots are in Figures 79 to 89. Methane is formed even at low temperatures and contact time indicating it to be a direct product of F-T processing, ethylene also seems to be a direct product. However, whereas methane does not seem to be consumed once formed, ethylene appears to be (curve bends down at higher contact times). Ethane appears to be a product of secondary synthesis (zero or near zero yield at low contact times, but rapid, non linear, yield increase at high contact times). Most logically ethane comes from hydrogenation of ethylene. Ethanol seems, at least in part, to result from direct synthesis. Propylene and butylene are direct products with some indication that they are consumed in secondary reactions. Propane and butane appear to be direct products whereas propanol and butanol appear to be products of secondary synthesis.

The effect contact time changes had on carbon monoxide and hydrogen conversion is expressed in Figure 89.

Three periods during this run were fully analyzed and Schulz-Flory plots were prepared (Figures 90 to 95). The values of α_1 varied from 0.65 to 0.69. The weight fractions of the total product in each of the historic fuel ranges appear in Figure 96.

At the end of the run the carbon monoxide conversion was 70% and the $C_1 + C_2$ selectivity was 5.2 mole %. This was approximately the same as the line out performance of the Run 37 (Figure 51) potassium carbonate-derived catalyst which was 5.2 mole % $C_1 + C_2$ selectivity at 73% carbon monoxide conversion. Although the performance was not improved over the earlier catalyst, potassium laurate did offer the promise of an easier catalyst preparation and work was continued on it. A tabular summary of the performance of the Runs 37, 42 and 43 catalysts is in Figure 97.

changes. However, slight decreases in both the methane and ethane selectivities were observed when the total potassium level was increased from 2.0 to 3.0 g/100 g $\cdot$ Fe (Figures 108 and 109). A summary plot of the response of conversions and selectivities to increases in potassium level appears in Figure 110. During the potassium laurate additions the ethylene selectivity decreased markedly from 4% to 2% (Figure 111). At three hundred and twenty-five hours on stream a significant amount of catalyst was lost from the reactor. This happened after both slurry filters plugged and the wax level had to be controlled by removal from the non-filtered outlet. After the catalyst loss the feed rate was decreased in order to increase the conversion back to the previous level. Although not labeled on Figure 105, the feed rate before this change was the usual 2.4 NL/hr $\cdot$ g Fe. Just before loss of catalyst the methane + ethane selectivity was 3.4 mole % at 70% carbon monoxide conversion! This is a very low selectivity, if catalyst had not been lost space velocity changes would have been made to allow determination of methane + ethane selectivities closer to the target CO + H₂ conversion of 88%. As with the previous run, high carbon dioxide selectivity was observed at low levels of potassium, whereas the major carbon monoxide increase occurred at higher levels of potassium.

The low methane + ethane selectivity and the fact that the conversion didn't decrease at total potassium levels greater than 2 g/100 g of iron indicate that use of potassium laurate during a run caused at least a somewhat different catalyst to form than from potassium carbonate. Propane/propylene and butane/butylene selectivities are in Figures 112 and 113.

Comparisons are made of the C₁->C₄ selectivities and olefin/paraffin ratios for the four potassium laurate runs in Figure 19. The methane + ethane selectivity was reasonably consistent at about 3.3 mole % when the high potassium catalysts of Runs 42, 46 and 49 were operated to produce 70%

carbon monoxide conversion. Extraordinary means were required to achieve this conversion during Runs 42 and 46 but not during Run 49. The high activity with a high potassium catalyst in Run 49 is also unique when compared to the catalysts described in Section 3.5.6. These earlier catalysts exhibited maximum conversion at about the 2 g/ 100 g iron level.

It is possible that potassium laurate is hydrolyzed to lauric acid and potassium hydroxide in the reactor before interacting with the catalyst. If that is the case other soluble organo-potassium salts should produce catalysts similar to the ones for potassium laurate. The runs in the next subsection were done with catalysts activated with such salts.

3.5.8 EVALUATION OF ADDITIONAL ORGANO-POTASSIUM COMPOUNDS

Potassium nonylphenolate and potassium benzoate were evaluated. In Run 63 potassium nonylphenolate was added intermittently as a solution in isopropanol/heptane to 72.3 grams a catalyst which contained 1.0 g of potassium carbonate-derived potassium/100 grams of iron (Figure 114). The catalyst appeared to have approached line out before potassium nonylphenolate addition started at ninety hours on stream; at this time the carbon monoxide conversion was 35%, and the methane and ethane selectivities were, respectively, 6.0 mole % (Figure 115) and 4.5 mole % (Figure 116). The metal oxide used was a fresh sample of the same one used in the previous Run 49. This run was performed under the same conditions but a solution of potassium laurate was added intermittently beginning at seventy-five hours on stream. Prior to these additions the catalyst was converting 40% of the carbon monoxide and exhibited methane and ethane selectivities of 6.8 and 3.5 mole % respectively (Figures 105, 108, and 109), although not exactly the performance in Run 63, it is close. Part of the difference is due to the selectivities not being completely lined out.

The potassium nonylphenolate additions did not produce the immediate and dramatic affect on performance that the potassium laurate additions did during Run 49. However, the qualitative affect of potassium nonylphenolate was in the same direction, namely increased conversions and decreased selectivities to light hydrocarbons. The catalyst did not appear to have fully lined out before addition of the potassium nonylphenolate. It is possible that the slow increase in activity after the first potassium nonylphenolate addition was just a continuation of the line out process. Both additions seemed to cause small decreases in methane selectivity. The first addition seemed to reduce the ethane selectivity somewhat, the second addition did not reduce it any further.

The difference between potassium laurate and potassium nonylphenolate addition is best illustrated by the following summary data. In Run 49, at 250 hours on stream and a total potassium level of 2.4 g/100 g of iron, the carbon monoxide conversion was 70%, and the methane and ethane selectivities were, respectively, 3.1 and 1.1 mole %. In Run 63, at 170 hours on stream and a total potassium level of 2.3 g/100 g of iron, the carbon monoxide conversion was only 50%, and the methane and ethane selectivities were, respectively, 5.0 and 2.1 mole %. Clearly potassium laurate was more effective.

The potassium laurate solution was added intermittently to Run 63 beginning at 230 hours on stream. The first such addition produced an immediate effect, after it the total potassium addition was 3.0 g/100 g of iron, the carbon monoxide conversion was 70%, and the methane and ethane selectivities were, respectively, 2.7 and 1.9. This methane selectivity was about the same as in Run 49 at a potassium level of 3.0 g/100 g of iron, but the 1.9 mole % ethane selectivity was higher (Run 49 ethane selectivity = 0.7 mole %). A final potassium laurate addition was made but operational difficulties forced the run to be stopped before the full affect of it could be ascertained. This

addition brought the total potassium level to 3.9 g/100 g of iron, and appeared to cause additional, but smaller, decreases in the methane and ethane selectivities which were 1.9 and 1.1 at run's end. A tabular summary of Runs 49 and 63 including $C_1 \rightarrow C_4$ selectivities is in Figure 117. During Run 63 the potassium laurate additions also caused a lowering of the propane/propylene and butane/butylene selectivities (Figures 118 and 119).

Potassium benzoate was added near the end of Run 65. This run employed 25 grams of "direct filtered" metal oxide from Run 32 of the oxide precipitation plant. Primarily, this run was part of the study of catalysts from identical precipitation runs outlined in Section 3.5.5. The run conditions are in this previous section, however, it should be reiterated here that solid potassium laurate was added to the reactor at start up. Catalyst performance before addition of potassium benzoate was earlier summarized in Figure 49. The autoclave runs are time-consuming to start and whenever possible attempts were made to obtain some extra knowledge after the primary run objectives were achieved. In this run one addition of potassium benzoate in isopropanol solution was made beginning at 270 hours on stream (Figure 120). Although the increase in total potassium was from 1.8 to 3.0 grams/100 grams of iron, the conversions were barely affected (Figure 121). The increases in light end selectivities (Figures 122 to 124) were due to the increased carbon dioxide selectivity; the uncorrected light ends selectivities were unchanged by the potassium benzoate addition. The increased carbon dioxide selectivity could have been due to the potassium benzoate catalyzing the Boudouard reaction to some extent.

The differences in the way the three organo-potassium compounds effect the catalyst must be related to the different types of anions present. The simplest explanation is that the benzoate and nonylphenolate solubilize the potassium to such an extent that it does not "find" the catalyst surface,

and is, in fact, eventually lost into the withdrawn product wax. However, there are other explanations such as effects of the anions on adsorbed potassium. These mechanisms can only be differentiated with additional experiments.

3.5.9 EFFECT OF CATALYST PARTICLE SIZE ON PERFORMANCE

A sample of the through 400 mesh metal oxide which resulted during sizing of the product from one of the two identical precipitation runs was compared to the sized (through 140 on 400 mesh) material. Summaries of oxide properties are in Figure 125 and performance data after line out is in Figure 126. The catalyst evaluation conditions are in Section 3.5.5.

The catalysts reached an apparent conversion line out after 125 hours on stream. At this time the carbon monoxide was about 40% from the through 400 mesh catalyst and 20% from the other one. Although selectivities from the coarse catalyst reached apparent line out at this time also, those from the through 400 mesh catalyst still were changing at the end of the 240 hour run. The finer mesh catalyst reached an apparent conversion line out after two hundred hours on stream when the carbon monoxide conversion was 39%. The through 140 on 400 mesh material reached an apparent conversion line out after 125 hours on stream when the carbon monoxide conversion was 20% (Figure 127). Of the two catalysts, the finer mesh one was more selective for light hydrocarbons, perhaps in part because the selectivities were obtained at a higher conversion.

The conversions from the two catalysts did not converge at line out as might have been expected if they were both attrited to the same mesh size by line out. The conversion difference between the two catalysts might indicate some diffusion resistance.

3.5.10 EVALUATION OF A METAL OXALATE-DERIVED CATALYST

One run was performed with a catalyst which resulted from decomposition of a mixture of iron and copper oxalates (Section 3.2.2). It was a very powdery material, its performance, therefore, was compared to that of the through 400 mesh oxide evaluated in Section 3.5.9. The physical properties and performance of these two oxides can be compared in, respectively, Figures 125 and 126. The performance data summarized in the latter Figure was after the oxalate-derived catalyst had lined out. Performance of these two materials as a function of hours on stream is in Figures 128-134. At the end of the run, the oxalate catalyst was slightly less selective for light products than the reference catalyst.

3.5.11 EVALUATION OF CARBON MONOXIDE-ACTIVATED CATALYSTS

Two runs were performed with carbon monoxide-activated catalysts. Each used a fresh 72.3 g sample of the same iron/copper/silicon oxide catalyst precursor, the properties of which are in Figure 20. In the first run the reactor was loaded with the oxide, 290 g of C₃₀ oil and 6.7 g of potassium laurate (2.4 g K/100 g Fe). In the second run no potassium laurate was present at start up but a solution of it was added later. Details of the catalyst activation procedure were outlined in Section 3.3.3 and Figures 21 and 22.

Compared to synthesis gas activation, carbon monoxide activation produced a more active catalyst. For instance, in the first run the carbon monoxide conversion appeared to have lined out at 90% at the end of the ninety-six hour run (Figure 135). Plant operational problems forced early

termination of this run. At run's end the carbon monoxide + hydrogen conversion was 85% which is very close to the contract target of 88%. However, the methane and ethane selectivities were very high, although the methane selectivity had not yet lined out and was decreasing somewhat as the catalyst aged (Figures 136 and 137). The propane and propylene selectivities also had not reached line out and were also decreasing as the catalyst aged (Figure 138). The on line gas chromatograph was not separating the butane and butylene during this run, therefore, these selectivities are not available. The light alcohol selectivities were very low as they were during runs with catalysts resulting from synthesis gas activation (Figure 139).

The activation procedure for the second run was the same as the first. Potassium laurate was not added at the beginning of the run, but it was added intermittently during the run as a solution in a 50 : 50 weight blend of heptane/isopropanol. The initial conversions were about the same as in the first run, but after the addition of potassium laurate started they increased slightly then decreased (Figure 140). The performance of the two carbon monoxide activated catalysts are compared at similar times on stream and conversions in tabular fashion in Figure 141. A complete set of selectivities vs. hours on stream are in Figures 141 to 146. The potassium laurate at levels much above 1.0 g/100 g Fe appeared to cause changes in selectivities. For instance, at a cumulative potassium level of 1.5 g/100 g of iron the ethylene selectivity began to increase, however, the ethane selectivity stayed relatively constant until the potassium level reached 2.1 g/100 g of iron after which it decreased.

After the final addition of potassium laurate the conversion decreased over about one hundred and eighty hours. The nature of the catalyst was apparently changing very slowly; similar line outs were noted during the first one hundred to two hundred hours of runs wherein synthesis gas activation

was employed. At the end of the run the catalyst activity was apparently lined out and still fairly high compared to catalysts from synthesis gas activation (82% vs. 69-73% for the best synthesis gas activated catalysts). However, the methane + ethane selectivity was still unacceptably high (Figure 141).

Although carbon monoxide activation produced very active catalysts, the methane + ethane selectivities were unacceptable for the objective of this contract which requires this selectivity to be ≤ 5 mole %. The usual way of minimizing light hydrocarbon selectivity, namely the addition of potassium to the catalyst composition, has, so far, not caused sufficient lowering of the methane + ethane selectivity.

3.5.12 EVALUATION OF A UCI CATALYST: CROSSOVER TO SLURRY

BUBBLE REACTOR

United Catalysts Inc. manufactured a large lot of metal oxide for the first slurry bubble reactor run at the LaPorte, Texas plant. A fresh aliquot from an 800 lb composite of this material was evaluated and compared to results from the run at LaPorte. The physical properties of this metal oxide are in Figure 147. The performance summary is in Figures 148 to 152 as a series of performance vs. hours on stream plots.

The catalyst activation was the standard one with synthesis gas. The initial operating conditions were 2.5 NL/Hr · g of Fe, 200 psig and 265° C. The catalyst was quite active, for instance, the carbon monoxide conversion was stable at 80% over the first two hundred hours of operation

(Figure 148). Operational problems resulted in loss of all selectivity data from one hundred to two hundred hours on stream, however at 100 hours the methane + ethane selectivity was a low 3.7 mole%. At two hundred hours the feed rate was doubled resulting in an immediate drop in the conversions, for instance, carbon monoxide conversion fell to 41%. At two hundred and fifty hours the pressure was increased to 400 psig. This increased the conversion, but appeared to cause loss of catalyst activity. Directly after the pressure increase the carbon monoxide conversion was 58%, but after one hundred and fifty hours at this pressure it was 44%. At four hundred hours on stream the initial operating conditions were restored; the conversions, however, did not recoup to their values at two hundred hours on stream, for instance, the carbon monoxide conversion was only 41%. During the final one hundred hours of operation the conversion did appear to be constant. The methane + ethane selectivity was 4.5 mole % at the end of the run.

4. RESULTS AND DISCUSSION

One objective of this contract was development of the means to prepare an iron-based LPFT catalyst at the rate of 100 lbs/day. This production rate has been met with a pilot plant which produces metal oxides via precipitation. For the catalyst preparation procedure developed, a high rate of filtration is essential. There is room for improvement in the current method through reducing the amount of water injected in the reactor and/or addition of higher capacity filters.

Catalyst evaluations were performed in a slurry autoclave pilot plant; good progress has been made toward achieving the catalyst performance targets. Means are not yet available to accurately predict how the performance in a slurry autoclave correlates with that in a slurry bubble reactor, however, in one case fresh samples of the same catalyst were evaluated in both the slurry autoclave reactor and the large slurry bubble reactor at LaPorte, Texas. There was pretty good correlation between the one stage of slurry processing and the bubble reactor from the standpoints of conversion and selectivity at the same temperature and feed rate. However, this must be confirmed by additional crossover experiments.

Slurry autoclave conversions with the best catalysts of this contract at target processing conditions were below the slurry bubble conversion target. However, the methane + ethane selectivities were well within the target limitations; this can probably be taken advantage of by processing at slightly higher than target temperatures and/or pressures to achieve higher conversions while still

maintaining target methane + ethane selectivity.

Potassium is a key component of the iron F-T catalyst; it influences both activity and selectivity. The way potassium works has been studied by many workers. In some work potassium has been added as potassium metal, particularly for work done on clean iron surfaces with potassium metal coverages up to about one monolayer. In other cases, such as actual F-T catalysts ionic potassium has been added. It should not be a surprise if these different types of potassium produce different results. During this contract means were developed to simplify addition of potassium ion. In so doing ways of achieving better selectivity control were also discovered.

There is considerable evidence from surface studies that carbon monoxide is adsorbed both intact and dissociatively by iron even at temperatures below those used for F-T processing. Private discussions with J. Rabo have expanded upon his findings during work leading to the two earlier-cited papers.^{14, 15} In this work he found that under F-T conditions iron and cobalt catalysts cause dissociation of about 80% of the carbon monoxide, whereas with palladium only 0.1% is dissociated.

One mechanism which has been given for dissociation involves back bonding of electrons from the metal d-band into an antibonding orbital of carbon monoxide, thus weakening the carbon-oxygen bond. Anything which enhances the d-band electron density, such as metallic potassium, will facilitate this backbonding. In addition, donation of electrons to the d-band will enhance the bonding of carbon and oxygen to the surface, also contributing to cleavage of the carbon-oxygen bond.

Many experiments have been done to elucidate the mechanism of the F-T reaction. Within the last

decade most workers seem to have concluded that the body of experimental evidence favors the dissociative mechanism of Rabo whereby the initial step is cleavage of carbon monoxide into iron carbide and iron oxide as above. Quite a bit is known about the subsequent steps, for instance, measurements have been made of initiation and propagation rates and very good product analyses have been done. However, the nature of these steps is not as clearly known as that of the initial step. An understanding of the factors which control the propagation step is particularly required to prepare more selective catalysts.

Hoffmann has attempted to close the dissociative mechanism with a series of steps resulting from careful development of a model based on extended molecular orbital theory. He involves the d-band electrons of the metal surface. Hoffmann does not discuss the role of potassium, however, an attempt will be made herein to understand how potassium affects the catalyst in terms of Hoffmann's picture.

According to Hoffmann, the critical propagation step is dependent upon the migration abilities of adsorbed alkyl and carbenoid species which result from hydrogenation of the metal carbide formed during the dissociation step. The migratory aptitudes are affected by the extent of filling of the metal d-band; Hoffmann's calculations indicate mobility is lower for higher d-band filling. Since longer carbon chains are expected from higher mobilities, and since in going from left to right across the transition metal series ($\text{Fe} \rightarrow \text{Co} \rightarrow \text{Ni}$) the d-band is being filled, one expects to see progressively shorter chains across this series. This is observed; nickel, in fact, is usually considered a methanation rather than an F-T catalyst.

One would like to understand the effect of potassium on the iron F-T catalyst in terms of the

Hoffmann model. It is known that potassium salts cause longer chains to form on iron. If only d-orbital filling needs to be invoked to explain this, then the effect caused by ionic potassium is to remove electrons from the d-band. Work cited above with potassium metal indicated that carbon-oxygen bond cleavage in carbon monoxide is facilitated by electron donation from potassium metal. If potassium salts do, on the other hand, subtract electron density from the metal d-band they cannot facilitate carbon-oxygen bond cleavage by the above mechanism. One must, therefore, derive an alternate explanation for the shift and F-T reaction rate enhancements observed in most cases from low to medium levels of potassium salts.

Contemporary thinking is that physisorption of carbon monoxide onto the working catalyst is slow compared to carbon-oxygen bond cleavage. In this context an increase in the overall rate would result from an increase in the rate of physisorption of carbon monoxide which, in turn, will depend upon the rate at which it can displace the species which cover the surface and which are expected to be mainly reaction products such as olefins. Carbon monoxide is more polar than those products which it has to replace. The flow of electrons from the iron d-band to potassium cation might make the surface less nucleophilic (basic) and reduce the ability of the surface to hold the relatively non-polar reaction products. This mechanism would have to be further modified to explain why high levels of potassium ion begin to cause loss in catalyst activity.

In the work with potassium laurate it was shown that low levels of potassium effectively catalyze the shift reaction but not the F-T reactions. This likely indicates a less complex active site for shift catalysis, for instance, one including just one potassium ion. Thus every potassium added initially can produce another active shift catalysis site. On the other hand, two or more potassiums in near proximity might be required for a F-T active site. Such sites would only begin to form in quantity

at relatively high levels of potassium.

The loss in activity with high levels of potassium carbonate-derived potassium might be due to loss of catalyst active sites by making them too concentrated in potassium, e. g., maybe two or three proximal potassium ions are good but four or more are bad. The key finding with potassium laurate was that even at high potassium levels activity was maintained. This indicates that the laurate anion, when it is present instead of the oxide anion, causes a change in catalyst properties, perhaps by sterically separating proximal potassiums. This certainly is not the only possible explanation. For instance, if cationic potassium effects activity and selectivity by an electron effect such as above, it stands to reason that different anions would have the ability to modify this electronic interaction.

Performance results during this contract are summarized in a set of conversion/selectivity plots attached as Figures 153 to 159. Such plots allow different catalysts to be compared in such a way that changes in selectivities with conversion are taken into account. It is known that at high conversion selectivities to light products increase. The hydrogen/carbon monoxide usage ratio is less than the feed hydrogen to carbon monoxide ratio, resulting in a hydrogen rich environment at high conversions. It is reasonable that this might favor formation of higher hydrogen content products such as low molecular weight hydrocarbons.

The key catalyst performance target of this contract is low methane + ethane selectivity (≤ 5 mole %) at high conversion (88% CO + H₂). The most important of the attached plots are, therefore, those which compare methane and ethane selectivities. For instance, Figure 153 contains data pertaining to methane selectivities for a series of catalysts resulting from use of either potassium

carbonate or laurate. High potassium levels result in the lowest methane selectivities. Unfortunately, high potassium also usually means lower activity necessitating heroic means such as above target temperatures or below target feed rates to achieve high conversion. However, one high potassium catalyst maintained high activity while still exhibiting low methane selectivity. It resulted from impregnation/calcination of a small amount of potassium (1 g : 100 g iron) followed by periodic additions of a solution of potassium laurate in isopropanol/heptane. This catalyst evinced a low ethane selectivity (Figure 154). It was superior to high potassium catalysts resulting only from impregnation/calcination of potassium carbonate or addition of potassium laurate, although in the latter case the superiority was only in conversion activity. The catalyst resulting from addition of a solution of potassium laurate to a potassium-free catalyst exhibited low methane selectivity at high potassium level and high conversion when the high conversion was obtained by increasing the temperature. This was surprising because temperature increases usually cause big increases in a catalyst's intrinsic methane selectivity, temperature increases, therefore, are usually avoided as a way to increase conversion.

Other selectivities are summarized in Figures 155 to 160. These show that the conclusions formed above with methane are similar to those with other paraffins up to butane. Alkene selectivities, on the other hand, do not seem to be affected much by the different methods of potassium addition.

A key finding of this phase of the work was that a combination of potassium carbonate impregnation/calcination followed by addition of a solution of potassium laurate resulted in low methane and ethane selectivities and also high activity even at high potassium levels. A second finding was that addition of all the potassium as a potassium laurate solution during a run produced a lower selectivity catalyst at a given conversion and potassium level than addition of all the

potassium as potassium carbonate. Unfortunately in this case the activity was low even at a high potassium level.

The use of other organo-potassium salts produced less striking results. Use of a solution of potassium nonylphenolate during a run with a catalyst initially containing 1.0 g potassium/100 g iron from potassium carbonate impregnation resulted in changes in conversions and selectivities that somewhat mirrored the changes due to addition of a solution of potassium laurate to a similar catalyst, however, the magnitudes of these changes were much smaller with potassium nonylphenolate. A potassium benzoate solution was also used in one run. In this case there was no change in the conversion or hydrocarbon products, but there was an increase in the selectivity to carbon monoxide.

Pretreatment with carbon monoxide resulted in more active catalysts than ones activated with synthesis gas. The reason for this is not clear although it is known from work using clean metal surfaces that different crystal planes have different abilities to catalyze bond cleavage, for instance, carbon-oxygen bond cleavage. It is possible that the iron carbide phase(s) present after carbon monoxide activation are different from the phase(s) present after synthesis gas activation. Presumably the University of Kentucky studies being done under their DOE contract will provide comparisons of the products from various types of iron oxide reductions via Moessbauer and other techniques.

The first of the two carbon monoxide activations was performed with potassium, as potassium laurate, present at the start. The second such activation had no potassium present at the start and, as expected, the catalyst was only slightly more selective for light end products. The activity with and without potassium, however, was not greatly different. The potassium laurate solution was

added intermittently during the run with the initially potassium-free catalyst. These additions initially resulted in slightly increased catalyst activities, but eventually appeared to cause activity loss. The maximum carbon monoxide conversion during the potassium additions was 93% which was the highest achieved during this work. During the potassium additions, as the conversion increased, a small decrease in the methane selectivity was noted, but there was virtually no change in the other light end product selectivities. Overall, potassium seems to have less affect on a carbon monoxide activated catalyst.

Conversion/selectivity plots comparing results from the earlier synthesis gas activation to the first of the carbon monoxide activations (C_1 , C_2 , and C_3 hydrocarbons) are in Figures 160 to 164. When plotted on this basis both the ethane and propane selectivities seem higher than would be expected from continuing the curve resulting from the earlier work when potassium laurate was added at the start with a synthesis gas activated catalyst. The methane selectivity, although high, appears to fall on the continuation of this earlier line. It would appear that carbon monoxide activation produces a fundamentally different material than synthesis gas activation.

5. CONCLUSIONS AND FUTURE DIRECTIONS

Iron/copper and iron/copper/silicon oxides produced by the simple precipitation pilot plant via mixing aqueous solutions of sodium carbonate and metal salts were acceptable precursors for iron-based F-T catalysts. The precipitation pilot plant runs were short due to the high rate of precipitate production and the relatively slow rate of the available filtration equipment. The best yields of precipitate resulted from presetting the rates of the aqueous feed solutions. Making feed rate changes during a run based on changes in the pH of the blended solution in the reactor didn't work. The feedback loop was too long for this to be successful for the short runs in this work. Although a start was made in determining how reproducible the properties of the precipitates were from run to run more such work would be useful.

A slurry autoclave pilot plant was used to evaluate the catalysts. Catalysts were made from the metal oxide precipitates by adding potassium and activating with either carbon monoxide + hydrogen or carbon monoxide alone, in either case the activation was done before the start of the run in the slurry autoclave reactor. In a few cases potassium was added to the reactor after the catalyst was activated and the evaluation run had begun. In this testing mode the target conversion was not achieved with any of the catalysts evaluated. However, this target was for performance in a slurry bubble reactor and good crossover data between the two reactors are not yet in hand. The target methane + ethane selectivity was achieved.

The best catalyst from the standpoint of high activity and low methane + ethane selectivity resulted from addition of potassium to an iron/copper oxide via potassium carbonate impregnation/calcination followed by activation with carbon monoxide + hydrogen and addition of potassium as a solution of potassium laurate.

Potassium laurate as a solid or in solution was an effective way to add potassium to the catalyst. In addition to allowing preparation of the superior catalyst above its method of use was such that the separate, time-consuming, potassium carbonate impregnation/calcination was eliminated.

There are many experiments that should be done with potassium laurate and other organo-potassium compounds. Foremost are experiments in which solid organo-potassium compounds are added at the beginning of a run (initially potassium laurate) followed by addition of a solution of the organo-potassium compounds (again, initially potassium laurate). Such experiments should have as objectives: determination whether the potassium carbonate impregnation/calcination (above) is required for the superior performance noted when potassium laurate is added during a run.

After completing additional work with potassium laurate, experiments should be performed to determine how other organo-potassium compounds effect the catalyst system. A few tentative experiments were performed during this contract with potassium benzoate and potassium nonylphenolate solutions. However, these were never added to the reactor as solids at the beginning of a run and other organo-potassium compounds were not evaluated. Addition at the beginning of a run would allow determination of whether or not the very small effects produced on the catalyst by potassium benzoate and potassium nonylphenolate are due to the salts being lost to the catalyst system though solubility in the product wax which is periodically removed from the reactor.

Although this is not the case with potassium laurate it could be with other organo-potassium compounds. On the other hand, if the small effect on catalyst performance due to these organo-potassium compounds results from them being unable to promote the iron other experiments are suggested. If this is the case, the anion along with the potassium ion plays a role at the catalyst active site. Many other organo-potassium compounds are available, some of which might be superior to potassium laurate. For instance, dicarboxylic acid salts and salts of acetylacetonate have not as yet been evaluated.

The special method of introduction of potassium during a run as a soluble organo-potassium salt should be extended to the addition of other salts such as those of copper and iron or mixtures thereof.

The most successful run was terminated because of operational problems before all of the planned potassium laurate solution was added. This run should be repeated to confirm that the very high activity is maintained at high levels of added potassium since that is one of the key findings of this work. Furthermore, more potassium laurate should then be added to determine whether the high activity persists at even higher potassium levels which might cause further reductions in the methane + ethane selectivity. Slightly more strenuous conditions might then allow target conversion to be attained at the target selectivity.

Finally, additional experiments should be done in which solutions of potassium laurate are added during the run. Initially the earlier very successful Run 49 (Figures 107 to 113) should be repeated but the addition of the potassium laurate at a different time (initially earlier) to determine whether even better results can be obtained. It is known that the catalyst undergoes changes during the

initial phases of a run, perhaps addition of potassium during this period will produce interesting results.

FIGURE 1

FIGURE 2

MAGNETIC PROPERTIES:
GROUP VIII METALS AND CARBIDES

MATERIAL	CURIE TEMP, °C	FISCHER-TROPSCH ACTIVITY
α -Fe	770	EXCELLENT
α -Co	1115	EXCELLENT
β -Co	1115	EXCELLENT
Ni	353	SOME, CH, GOOD
Ru	PARAMAGNETIC	EXCELLENT
Rh	PARAMAGNETIC	POOR
Pd	PARAMAGNETIC	POOR
Os	PARAMAGNETIC	POOR
Ir	PARAMAGNETIC	POOR
Pt	PARAMAGNETIC	POOR
Fe_3C	210	EXCELLENT
ϵ - Fe_3C	380	EXCELLENT
X- Fe_3C	247	EXCELLENT
FeC	250	EXCELLENT
Ni_3C (hcp)	PARAMAGNETIC	INERT
Ni_4C	220	SOME

FIGURE 3**Slurry Bubble Demonstrations**

Plants	Rheinprussen Plant	Mobil (Low Wax)	Mobil (High Wax)
Temp., °C	268	260	258
Pressure, psig	176	221	221
SV, NL/kgFe/hr	3,400	2,600	2,400
CO+H₂ Conv., %	89.0	86.8	82.2
Product Yield, gHC/gFe/hr	0.57	0.37	0.41

PLT 752

FISCHER-TROPSCH CATALYST PRECIPITATION

FIGURE 4

FIGURE 5
F-T CATALYST PREPARATION REACTOR

FIGURE 6
PHOTOGRAPHS OF PLANT 752

FIGURE 7

TYPICAL PREPARATION CONDITIONS
for PPTD. Fe CATALYSTS

- **Fe/Na₂CO₃ Mole Ratio = 0.65**
- **Feed Solns.**
 - **Fe/Cu 5.0% Fe, 0.15% Cu (Nitrates)**
 - **Na₂CO₃ 5.3%**
 - **SiO₂ 0.1% (to Na₂CO₃ , as Na₂SiO₄)**
- **Feed Rates**
 - **Fe/Cu Soln. 115 g/min**
 - **Carbonate Soln. 315 g/min**
 - **Water 400 g/min**
- **25°C, pH 5.0-5.5, 3-4 Hr Duration**
- **Production Rate ~500g Fe₂O₃ /Hr**
 - **Pptn. Zone Solids ~2 Wt%**
 - **Outlet Solids ~1 Wt%**

FIGURE 8

F-T CATALYST PLANT 752
RUN 32 - FEED RATES

F-T CATALYST PLANT 752
RUN 32 - pH READINGS

FIGURE 9

**F-T CATALYST PLANT 752
RUN 33 - FEED RATES**

**F-T CATALYST PLANT 752
RUN 33 - pH READINGS**

FIGURE 10

PLANT 752 PRECIPITATION STEP Fe, Cu, Si WEIGHT BALANCE

RUN #	30	32	33
<u>FEED ANALYSIS</u>			
Fe/Cu SOLUTION Fe WT %	5.04	4.47	5.07
Fe/Cu SOLUTION Cu WT %	0.17	0.159	0.167
Na SOLUTION Na WT%	NA	2.35	2.44
Na SOLUTION Si PPM	-	-	532
<u>WEIGHTS FED</u>			
Fe/Cu SOLUTION, g	17,444	29,984	21,819
Na SOLUTION, g	NA	NA	58785
Fe, g	879.18	1340.28	1106.22
Cu, g	29.65	47.67	36.44
Si, g	-	-	31.3
<u>WEIGHT RECOVERED</u>			
<u>(AS DRIED SOLID)</u>			
DIRECT FILTERED, g	827.04	880.50	898.76
LOI, WT%	16.56	12.91	14.28
Fe, WT% VF	66.30	65.70	64.80
Cu, WT% VF	2.26	2.27	2.15
Si, WT% VF	.20	-	1.35
OVERFLOW FILTERED, g	414.82	1205.30	903.20
LOI, WT%	16.91	14.37	13.89
Fe, WT% VF	66.00	66.20	64.60
Cu, WT% VF	2.27	2.39	2.19
Si, WT% VF	.12	-	1.74
SUM Fe, g	685.06	1187.05	1001.65
SUM Cu, g	23.42	42.07	33.60
SUM Si, g	0.18	-	23.9
<u>WEIGHT BALANCE</u>			
Fe, WT%	77.92	88.57	90.55
Cu, WT%	78.98	88.25	92.20
Si, WT%	-	-	76.4

FIGURE 11
F-T PPTD. Fe CATALYST
Plt. 752/Run 32

FIGURE 12

FIGURE 13

WORK-UP of PLT 752 PRECIPITATED CATALYST

F-T Fe CATALYST YIELD
% Yield After Grinding and Sizing,
On Calcined Catalyst Basis

FIGURE 14

CATALYST PREPARATION STUDY

PHYSICAL PROPERTIES

Fe/Cu OXIDES FROM CATALYST PREPARATION PLANT	METALS, WT%			Na, ppm	BET	
	Fe	Cu	Si		SA, m²/g	PV, cc/g
RUN 30, DIRECT	65.5	2.1	N/A	47	97	0.47
RUN 30, OVERFLOW	66.0	2.3	N/A	<100	108	0.44
RUN 32, DIRECT	64.5	2.2	N/A	19	133	0.30
RUN 32, OVERFLOW	64.3	2.3	N/A	<100	157	0.36
RUN 33, DIRECT	62.5	2.1	1.3	31	244	0.29
RUN 33, OVERFLOW	60.0	2.1	1.3	<100	257	0.29

STEM ANALYSIS: RUN 30

FIGURE 16

OVERFLOW FILTERED

DIRECT FILTERED

STEM ANALYSIS: RUN 32

FIGURE 17

OVERFLOW FILTERED

DIRECT FILTERED

RUN 11 6753 119

INTENSITY (CPS) #100

FILE XRD5FX1: 938538.X1 CREATED ON 19-AUG-1993

19-AUG-93 14:21:17

2THETA STEP TIME (SEC) = 2.02
2THETA STEP SIZE (DEG) = 0.040
INSTRUMENT # 4

- * ① Fe_5C_2 #20-500
 * ② $Fe_{2.5}C$ #96-1348
 * ③ Fe_2C #17-897 (possible)
 * ④ Fe_2C 36-1344 (possible)
 * ⑤ FeC 6-486 possible
 or Fe_3C_2 17-533
 * ⑥ h. hematite 40-1445
 * ⑦ Fe 6-496 (possible)
 * ⑧ FeC 3-419 (possible)
 * ⑨ Fe_3C 38-772 (possible)

FIGURE 18

**THE FOUR POTASSIUM LAURATE RUNS:
PERFORMANCE AT STANDARD CONDITIONS**

RUN NO.	42	43		46	49
MODE OF K ADDITION	SOLID K LAURATE			K LAURATE IN SOLUTION	K ₂ CO ₃ + K LAURATE IN SOLUTION
TOTAL K, g/100 g Fe	3.6	2.1		3.7	3.0
CO CONVERSION, %	70 ¹	73	81 ¹	70 ²	70
SELECTIVITIES					
C ₂ ² /C ₃	2.5	4.1	4.5	2.6	2.7
C ₃ ² /C ₄	0.8	1.1	1.9	0.8	0.7
C ₄ ² /C ₅	2.5	2.7	2.9	2.7	2.1
C ₅ ² /C ₆	0.6	1.0	1.1	0.5	0.6
C ₆ ² /C ₇	3.9	4.7	5.5	4.0	3.8
C ₇ ² /C ₈	0.6	1.0	1.1	0.3	0.6
C ₈ ² /C ₉	2.8	3.4	3.9	3.0	2.8
OLEFIN/PARAFFIN RATIO					
C ₂ ² /C ₃	3.1	2.5	1.5	3.4	3.0
C ₃ ² /C ₄	6.5	4.7	5.0	8.0	6.3
C ₄ ² /C ₅	4.7	3.4	3.5	10.0	4.7

1. SPACE VELOCITY WAS LOWERED FROM STANDARD 2.4 NL/hr • g Fe.
2. TEMPERATURE WAS INCREASED TO 290° C FROM STANDARD 265° C.

FIGURE 19

METAL OXIDE USED FOR RUNS WITH CARBON MONOXIDE ACTIVATION

OXIDE PREP PLT NO.	AUTOCLAVE PLT RUN NO.	MESH RANGE	METALS, WT% (AS REC'D)			BET	
			Fe	Cu	Si	SA, m ² /g	PV, cc/g
33	71	-140 + 400	55.6	2.12	1.25	244	30
	72						

FIGURE 20

PLANT 701 RUN 71 CO2 DURING ACTIVATION

FIGURE 21

PLANT 701 RUN 72 CO2 DURING ACTIVATION

FIGURE 22

FIGURE 23

Moessbauer of Fischer Tropsch Catalysts

Composition vs Hour on Stream Run 32

FIGURE 24

FIGURE 25
DIFFRACTION PATTERNS FOR FISCHER-TROPSCH SLURRY AS A FUNCTION
OF REACTION TIME

FIGURE 26

TYPICAL SUSCEPTIBILITY CURVE FOR CARBIDIC IRON SPECIES

(SIGMA/SIG.20K).S# 6616-49.81, RUN #32
 1000 Gauss, CATALYST+WAX, 0-47 HOS

FIGURE 27

FIGURE 28

ATTRITION OF Fe CATALYST
Particle Size by Laser Light
Scattering, After Sonic Probe Mixing
(AQUEOUS SLURRY)

FT-DOE10

PLT 701.
RUN#—

FIGURE 29

HOT BOX

168 2ND ENTERED G.P.S
'HACE ANTIET BLOCK VANE

Schematic of Slurry Autoclave Plant

FIGURE 30

UOP 2146-27

FIGURE 31

PLT 701

AUTOCLAVE 1 LTR

RUN NO. _____

CATALYST GMS: _____ CC'S: _____ CATALYST NO. _____

CATALYST DESCRIPTION: _____

WAX GMS: _____ CC'S: _____

MEASURE TC TO _____

OXIDE USED FOR SLURRY AUTOCLAVE CERTIFICATION

PHYSICAL PROPERTIES

Fe/Cu OXIDE CATALYST PREP PLANT RUN NUMBER	METALS, WT%		Na, ppm	BET	
	Fe	Cu		SA, m²/g	PV, cc/g
17	58.3	2.4	<100	79	0.21

FIGURE 33 COMPARISON OF RUNS 28, 29 & 30, CATALYST 6616-49

$H_2:CO$ feed = 0.7, 1100 rpm
CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 Δ
RUN 29 $\square$
RUN 30 $\circ$

FIGURE 34

COMPARISON OF RUNS 28, 29 & 30, CATALYST 6616-49

$H_2:CO$ feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 Δ
 RUN 29 $\square$
 RUN 30 $\circ$

FIGURE 35

COMPARISON OF RUNS 28, 29 & 30, CATALYST 6616-49

$H_2:CO$ feed = 0.7, 1100 rpm
 CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 Δ
 RUN 29 $\square$
 RUN 30 $\circ$

FIGURE 36

COMPARISON OF RUNS 28, 29 & 30, CATALYST 6616-49

$H_2:CO$ feed = 0.7, 1100 rpm
CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 Δ
RUN 29 $\square$
RUN 30 $\circ$

FIGURE 37

COMPARISON OF RUNS 28, 29 & 30, CATALYST 6516-49

H₂:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C₃₀ oil

RUN 28 Δ
 RUN 29 $\square$
 RUN 30 $\circ$

FIGURE 38

COMPARISON OF RUNS 28, 29 & 30, CATALYST 6616-49

H₂:CO feed = 0.7, 1100 rpm
 CATALYST 752R17B7 72.7g cat, 290g C₃₀ oil

RUN 28 Δ
 RUN 29 □
 RUN 30 ○

FIGURE 39 **COMPARISON OF RUNS 28, 29 & 30, CATALYST 6615-49**

$H_2:CO$ feed = 0.7, 1100 rpm
 CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 Δ
 RUN 29 $\square$
 RUN 30 $\circ$

RUHR CHEMIE OXIDE
PHYSICAL PROPERTIES

SOURCE OF CATALYST	METALS, WT %, V.F.				Fe:K (WT)	BET	
	Fe	Cu	Si	K		SA, m ² /g	PV, cc/g
RUHR CHEMIE	43.8	2.2	4.8	1.35	100 : 3.1	313	0.53

FIGURE 41
RUHR CHEMIE REFERENCE CATALYST
 PLI 700B RUN 31 $H_2:CO$ feed = 0.7, 1100 rpm
 72.7g cat, 290g C_{30} oil

FIGURE 42
RUHR CHEMIE REFERENCE CATALYST
 PLT 700B RUN 31 $H_2:CO$ feed = 0.7, 1100 rpm
 72.7g cat, 290g C_{30} oil

FIGURE 43
RUHR CHEMIE REFERENCE CATALYST
 PLT 700B RUN 31 $H_2:CO$ feed = 0.7, 1100 rpm
 72.7g cat, 290g C_{30} oil

FIGURE 44

RUHR CHEMIE REFERENCE CATALYST
 PLI 700B RUN 31 H₂:CO feed = 0.7, 1100 rpm
 72.7g cat, 290g C₃₀ oil

FIGURE 45
RUHR CHEMIE REFERENCE CATALYST
 PLT 700B RUN 31 $H_2:CO$ feed = 0.7, 1100 rpm
 72.7g cat, 280g C_{30} oil

FIGURE 46

RUHR CHEMIE REFERENCE CATALYST

PLT 700B RUN 31 $H_2:CO$ feed = 0.7, 1100 rpm

72.7g cat, 290g C_{30} oil

FIGURE 47

RUHR CHEMIE REFERENCE CATALYST

PLT 700B RUN 31 $H_2:CO$ feed = 0.7, 1100 rpm

72.7g cat, 290g C_{30} oil

FIGURE 48

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R-62 25g 6827-104 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm

CATALYSTS FROM IDENTICAL PRECIPITATION RUNS
PERFORMANCE COMPARISON AT LINE OUT

FIGURE 49

AUTOCLAVE RUN NO.	58	62	65	68
PRECIP FLT NO./ HOW FILTERED	30/DIRECT	30/OVERFLOW	32/DIRECT	32/OVERFLOW
CONV., %				
CO	20	28	40	46
H ₂	20	25	38	40
CO + H ₂	22	29	39	42
H ₂ /CO USAGE	0.65	0.60	0.68	0.60
SELECTIVITIES				
CO ₂	42	48	48	48
C ₁	1.8	2.9	3.6	3.5
C ₂	0.1	0.5	0.7	0.8
C ₃	0.8	3.0	3.6	4.5
C ₄	.85	0.7	0.9	0.8
C ₅	2.7	3.5	4.4	4.3
C ₆	0.0	0.0	0.0	0.0
C ₇	1.5	1.5	3.0	3.3

FIGURE 50**Properties of Oxides**

Run No.	Oxide after K_2CO_3 , Fe:Cu:K:Si, wt	Surface Area, m^2/g	Pore Volume, cc/g
35	100:2.05:2.37:1.16	192	0.24
36	100:2.31:2.41:1.72	196	0.25
37	100:2.10:2.31:2.06	187	0.23
39	100:2.46:2.25:2.70	193	0.23
38	100:2.13:2.22:3.85	179	0.22

FIGURE 51**Effect of Potassium Level on Iron Catalyst Performance**

Catalyst Fe:K, wt	Feed Rate NL/gFe/hr	Line-Out Results ^a			
		CO Conv., %	Carbon Selec., mol-%		H ₂ /CO, ^b Molar
			C ₁ +C ₂	C ₂ =	
100:1.16 (Run 35)	2.7	73	8.5	2.0	0.90
100:1.72 (Run 36)	2.4	73	8.4	2.2	0.90
100:2.06 (Run 37)	2.4	73	5.2	2.8	1.0
100:2.70 (Run 39)	2.4	50	3.6	2.6	0.78
	1.2	73	4.4	2.7	1.03
100:3.85 (Run 38)	2.4	50	3.0	2.9	0.72
^a 130 HOS					
^b At reactor outlet					

Effect of K Level on Conversion

FIGURE 52

Methane and Ethane Selectivities

Olefin : Paraffin Ratios at 73% CO Conversion

FIGURE 54

FIGURE 55**Comparison of CO₂ Selectivities**

Catalyst Fe:K, wt	Feed Rate NL/gFe/hr	CO Conv., %	Line-Out CO ₂ Selec., mol-%
100:1.16 (Run 35)	2.7	73	45.5
100:1.72 (Run 36)	2.4	73	45.5
100:2.06 (Run 37)	2.4	73	46.5
100:2.70 (Run 39)	2.4	46	45.0
	1.2	73	46.2
100:3.85 (Run 38)	2.4	55	44.8
* 130 HOS			

Alcohol Selectivities at 73% CO Conversion

FIGURE 56

Schulz-Flory Plots

Liq. by Off-Line and Gas by On-Line Analysis

UD-7001-1-80

FIGURE 58

Schulz-Flory Distribution

HC PRODUCT DISTRIBUTION PLANT 700B RUN 37

FIGURE 59

METAL OXIDES USED FOR FOUR RUNS WITH POTASSIUM LAURATE

OXIDE PREP PLT NO.	AUTOCLAVE PLT RUN NO.	MESH RANGE	METALS, WT% (AS REC'D)			LOI @ 500° C	BET	
			Fe	Cu	K		SA, m ² /g	PV, cc/g
19 ¹	42	-140 + 400	62.2	1.3	N/A	4.55	220	0.24
	43							
	46		60.7	0.7	N/A		212	0.24
	49 (AFTER K IMP)		62.8	0.8	0.6		197	0.22

1. SEVERAL LOTS WERE MADE DURING WORKUP OF RUN 19. ONE LOT FURNISHED MATERIAL FOR AUTOCLAVE RUNS 42 AND 43, AND ANOTHER FURNISHED MATERIAL FOR AUTOCLAVE RUNS 46 AND 49.

FIGURE 60

FIGURE 61

POTASSIUM LAURATE ADDITION TO SLURRY

PLJ 700B RUN 42 $H_2:CO$ feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.63 K ; 72.7g Fe/Cu Oxide+10g K Salt in 290 g C_{30} oil

FIGURE 62

POTASSIUM LAURATE ADDITION TO SLURRY

PLJ 700B RUN 42 $H_2:CO$ feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.83 K : 72.7g Fe/Cu Oxide+10g K Salt in 290 g C_{30} oil

FIGURE 63

POTASSIUM LAURATE ADDITION TO SLURRY

PLJ 700B RUN 42 H₂:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.83 K : 72.7g Fe/Cu Oxide+10g K Salt in 290 g C₃₀ oil

FIGURE 64

POTASSIUM LAURATE ADDITION TO SLURRY

PLJ 700B RUN 42 H₂:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.2 K : 72.7g Fe/Cu Oxide+10g K Salt in 290 g C₃₀ oil

TARGET TEMP, C
FEED, NL/H g Fe
PRESSURE, PSIG

GC2 C4
GC2 C1
GC2 C3
GC2 C3
PAR SELECTIVITY OLE SELECTIVITY PAR SELECTIVITY OLE SELECTIVITY

FIGURE 65

POTASSIUM LAURATE ADDITION TO SLURRY

PJ 700B RUN 42 H₂:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.2 K : 72.7g Fe/Cu Oxide+10g K Salt in 290 g C₃₀ oil

FIGURE 66

NONLINEAR REGRESSION OF F-T PROD. DIST
PLANT 700B, RUN 42, PERIOD 3

□ Experimental —●— NLR Fitted

ALPHA 1=0.63; ALPHA 2=0.91; XI=6.6;
PHI=0.458
\\RUN42\\P3NLR.CH

FIGURE 67

NONLINEAR REGRESSION OF F-T PROD. DIST
PLANT 700B, RUN 42, PERIOD 6

ALPHA 1=0.65; ALPHA 2=0.94; XI=7.2;
PHI=0.672
\\RUN42\\P6NLR.GHT

FIGURE 68

NONLINEAR REGRESSION OF F-T PROD. DIS
PLANT 700B, RUN 42, PERIOD 8

□ Experimental —●— NLR Fitted

ALPHA 1=0.64; ALPHA 2=0.96; XI=10.4;
PHI=2.672
\\RUN42\\P8NLR.GHT

IRON AND POTASSIUM IN WITHDRAWN WAX

RUN NO.	PERIOD NO.	HOURS ON STREAM	WAX ANALYSES, AAS		
			Fe, WT%	K, WT%	Fe : K (WT)
42	1	0-12	0.35	0.0142	100 : 4.1
42	2	13-36	0.21	0.0101	100 : 4.8
42	3	37-60	0.32	0.0357	100 : 11.2
43	1	0-12	1.75	0.0643	100 : 3.7
43	2	13-36	0.18	0.0112	100 : 6.2
43	3	37-60	0.49	0.0290	100 : 5.9

FIGURE 69

FIGURE 70

POTASSIUM LAURATE ADDITION TO SLURRY

PLJ 700B RUN 43 $H_2:CO$ feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K : 72.7g Fe/Cu Oxide+8.5g K Sulf In 290 g C30 oil

FIGURE 71

POTASSIUM LAURATE ADDITION TO SLURRY

PLJ 700B RUN 43 H₂:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K : 72.7g Fe/Cu Oxide+8.5g K Salt in 280 g C₃₀ oil

FIGURE 72

POTASSIUM LAURATE ADDITION TO SLURRY

PLJ 700B RUN 43 H₂:CO feed=0.7, 1100 rpm

100g Fe: 2.15 Cu: 2.1 K: 72.7g Fe/Cu Oxide+8.5g K Salt in 200 g C₃₀ oil

FIGURE 73

POTASSIUM LAURATE ADDITION TO SLURRY

PLI 700B RUN 43 H₂:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K : 72.7g Fe/Cu Oxide+8.5g K Salt in 290 g C₃₀ oil

FIGURE 74

POTASSIUM LAURATE ADDITION TO SLURRY

PLI 700B RUN 43 H₂:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K : 72.7g Fe/Cu Oxide+8.5g K Salt in 290 g C₃₀ oil

GC2 C4
GC2 C4
GC2 C3
GC2 C3
PAR SELECTIVITY
OLE SELECTIVITY
PAR SELECTIVITY
OLE SELECTIVITY

POTASSIUM LAURATE ADDITION TO SLURRY

PLJ 700B RUN 43 $H_2:CO$ feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K : 72.7g Fe/Cu Oxide + 8.5g K Salt in 290 g C30 oil

100g Fe : 2.15 Cu : 2.1 K : 7.2/8 H₂O : 0.25

FEED, NL/H/g Fe 2.0 ← 2.4 → 2.2 → 3.0 3.2 3.8 1.2 → 0.7 10.3 10.0 2.0 2.4

TARGET TEMP, C 280 ← 265 → 255 → 265

PRESSURE, PSIG 153 ← 210 →

ಹೆಚ್

GC1 C1

33 139

132

ALC SELECTIVITY ALC SELECTIVITY ALC SELECTIVITY ALC SELECTIVITY

FIGURE 76

Plant 700B, Run 43
CO Conv/Methane Sele

ETHANE SELECTIVITY/CONVERSION RUN 43

FIGURE 71

AFFECT OF CO + H2 CONV ON H2/CO USAGE RUN 43

265 DEG C

□ RUN 43

FIGURE 78

FIGURE 79

**Plant 700B, Run 43
Contact Time/Methane Yield**

FIGURE 80

Plant 700B, Run 43
Contact Time/Ethylene Yield

Plant 700B, Run 43
Contact Time/Ethane Yield

FIGURE 81

Plant 700B, Run 43
Contact Time/Ethanol Yield

FIGURE 82

Plant 700B, Run 43
Contact Time/Propene Yield

FIGURE 83

Plant 700B, Run 43
Contact Time/Propane Yield

Plant 700B, Run 43
Contact Time/Propanol Yield

FIGURE 85

Plant 700B, Run 43
Contact Time/Butene Yield

FIGURE 86

Plant 700B, Run 43
Contact Time/Butane Yield

FIGURE 87

Plant 700B, Run 43
Contact Time/Butanol Yield

FIGURE 88

Plant 700B, Run 43
Contact Time/Conversion

FIGURE 89

FIGURE 90

NONLINEAR REGRESSION OF F-T PRODUCTS PLANT 700B, RUN 43, PERIOD 4

□ Experimental — NLR Fitted

ALPHA 1=0.65; ALPHA 2=0.91; XI=7.2;
PHI=0.295
\\RUN43\\P4NLR.CHT

FIGURE 91

SCHULZ-FLORY DISTRIBUTION
PLANT 700B, RUN 43, PERIOD 4

\\RUN43\\P4EXP.CHT

FIGURE 92

**NONLINEAR REGRESSION OF F-T PRODUCT
PLANT 700B, RUN 43, PERIOD 9**

□ Experimental — NLR Fitted

ALPHA 1=0.65; ALPHA 2=0.96; XI=14.9;
PHI=0.122
\\RUN43\\P9NLR.CHT

FIGURE 93

SCHULZ-FLORY DISTRIBUTION
PLANT 700B, RUN 43, PERIOD 9

\\RUN43\\P9EXP.CHT

FIGURE 94

NONLINEAR REGRESSION OF F-T PRODUCTS PLANT 700B, RUN 43, PERIOD 15

ALPHA 1=0.69; ALPHA 2=0.94; XI=10;
PHI=1.091
\\RUN43\\P15NLR.CHT

FIGURE 95

SCHULZ-FLURY DISTRIBUTION
PLANT 700B, RUN 43, PERIOD 15

□ Experimental

\\RUN43\\P15EXP.CHT

HC PRODUCT DISTRIBUTION PLANT 700B RUN 43

FIGURE 96

\RUN43\GRPDIS.CHT

FIGURE 97

**PERFORMANCE SUMMARY: TWO POTASSIUM ADDITION METHODS
(LINED OUT CATALYSTS)**

PLT/RUN NO.	701/37	701/42	701/43
K ADD. METHOD	K ₂ CO ₃ IMPREG.	SOLID K LAURATE TO RX AT STARTUP	
CATALYST			
OXIDE PART, g	73	73	73
Fe, WT %	64.2	62.2	62.2
K, WT %	1.3	0.0	0.0
Fe:K, WT	100 : 2.1	—	—
K LAURATE, g		10	6.5
Fe:K, WT (TOTAL)	100 : 2.1	100 : 3.2	100 : 2.1
TEST CONDS.			
TEMP, °C	265	265	265
PRESS, PSIG	290	290	290
FEED RATE, (NL/HR · g Fe)	2.4	1.4	2.4
PERFORM. SUM.			
CONVER, %			
CO	76	70	70
H ₂	62	58	60
PRODUCTIVITY (M CO/HR · g AT. Fe)	2.5	1.4	2.3
SELEC., MOLE %			
C ₁	3.8	2.5	4.1
C ₂	1.9	2.7	1.1
(C ₁ + C ₂) —>	4.8	3.2	5.2
C ₂ °	3.0	2.5	2.7
CO ₂	47	45	47

1. FROM K₂O₃ IMPREGNATION

FIGURE 98

POTASSIUM FREE CATALYST/INTERMITTENT K-LAURATE ADDITION (K-LAURATE 0.03g / 10g 50:50(W) HEPTANE : ISOPROPANOL)

PLI 700B RUN 46 H₂:CO (M) feed=0.7, 1100 rpm. (1/27---->2/17/92)

100g Fe : 1.23 Cu ; 72.7g CAT. In 290 g C₃₀ oil

CUMULATIVE
GMS K/100g Fe

CO + H₂
CONVERSION

GC2 C1
SELECTIVITY

CO₂
SELECTIVITY

HOURS ON STREAM
177

FIGURE 99

POTASSIUM FREE CATALYST/INTERMITTENT K-LAURATE ADDITION
(K-LAURATE 0.03g / 10g 50:50(W) HEPTANE : ISOPROPANOL)

PLI 700B RUN 46 H₂:CO (M) feed=0.7, 1100 rpm. (✓27--->2/7/92)

100g Fe : 1.23 Cu : 72.7g CAT. In 290 g C₃₀ oil

FIGURE 100

POTASSIUM FREE CATALYST/INTERMITTENT K-LAURATE ADDITION
 (K-LAURATE 0.03g / 10g 50:50(W) HEPTANE : ISOPROPANOL)
 PLI 700B RUN 46 H₂:CO (M) feed=0.7, 1100 rpm. (1/27---->2/17/92)
 100g Fe : 123 Cu : 72.7g CAT. In 290 g C₃₀ oil

FIGURE 101

POTASSIUM FREE CATALYST/INTERMITTENT K-LAURATE ADDITION (K-LAURATE 0.03g / 10g 50:50(W) HEPTANE : ISOPROPANOL)

PLI 700B RUN 46 H₂:CO (M) feed=0.7, 1100 rpm. (✓27--->2/17/82).
100g Fe : 1.23 Cu : 72.7g CAT. In 290 g C₃₀ oil

FIGURE 102

POTASSIUM FREE CATALYST/INTERMITTENT K-LAURATE ADDITION (K-LAURATE 0.03g / 10g 50:50(W) HEPTANE : ISOPROPANOL)

PLI 700B RUN 46 H₂:CO (M) feed=0.7, 1100 rpm. (1/27--->2/17/92)

CUMULATIVE
GMS K/100g Fe

CO + H₂
CONVERSION

GC2 C₃
OLE SELECTIVITY

GC2 C₃
OLE SELECTIVITY

FIGURE 103

POTASSIUM FREE CATALYST/INTERMITTENT K-LAURATE ADDITION (K-LAURATE 0.03g / 10g 50:50(W) HEPTANE : ISOPROPANOL)

PLI 700B RUN 46 H₂:CO (M) feed=0.7, 1100 rpm. ($\sqrt{27}$ ---> 2/17/92)

100g Fe : 1.23 Cu : 72.7g CAT. In 290 g C₃₀ oil

FIGURE 104

POTASSIUM FREE CATALYST/INTERMITTENT K-LAURATE ADDITION (K-LAURATE 0.03g / 10g 50:50(W) HEPTANE : ISOPROPANOL)

PLI 700B RUN 46 H₂:CO (M) feed=0.7, 1100 rpm. (✓27--->2/17/92)

100g Fe : 1.23 Cu : 72.7g CAT. In 290 g C30 oil

CO + H₂
CONVERSION

GC1 C2
SELECTIVITY

GC1 C3
SELECTIVITY

C02
SELECTIVITY

HOURS ON STREAM
183

EFFECT OF K LEVEL ON CAT PERFORMANCE **NO INITIAL K ON CATALYST** **K LAURATE ADDED DURING RUN**

DATA AT 265 DEG C

FIGURE 105

FIGURE 107

PLT 700B RUN 49 INTERMITTENT CO-FEED POTASSIUM

72.7g 6827-17 in 290g C₃₀ oil

0.0405 wt% K-LAURATE in 50/50 IPA/HEPTANE

FIGURE 106

PLT 700B RUN 49 INTERMITTENT CO-FEED POTASSIUM

72.7g 6827-17 in 290g C₃₀ oil

0.0405 wt% K-LAURATE in 50/50 IPA/HEPTANE

♦ PARTIAL SLURRY LOSS

FIGURE 108

PLT 700B RUN 49 INTERMITTENT CO-FEED POTASSIUM

72.7g 6827-17 in 290g C₃₀ oil

0.0405 wt% K-LAURATE in 50/50 IPA/HEPTANE

FIGURE 109

PLT 700B RUN 49 INTERMITTENT CO-FEED POTASSIUM

72.7g 6827-T7 in 290g C₃₀ oil

0.0405 wt% K-LAURATE in 50/50 IPA/HEPTANE

● PARTIAL SLURRY LOSS

TEMPERATURE, °C
PRESSURE, psig
FEED RATE, SCFH

Effect of K Level on Cat Performance Run 49

FIGURE 110

FIGURE 111

PLT 700B RUN 49 INTERMITTENT CO-FEED POTASSIUM

72.7g 6827-17 in 290g C₃₀ oil

0.0405 wt% K-LAURATE in 50/50 IPA/HEPTANE

* PARTIAL SLURRY LOSS

FIGURE 112

PLT 700B RUN 49 INTERMITTENT CO-FEED POTASSIUM

72.7g 6827-17 in 290g C₃₀ oil

0.0405 wt% K-LAURATE in 50/50 IPA/HEPTANE

FIGURE 113

PLT 700B RUN 49 INTERMITTENT CO-FEED POTASSIUM

72.7g 6827-17 in 290g C₃₀ oil

0.0405 wt% K-LAURATE in 50/50 IPA/HEPTANE

FIGURE 114

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R-63 72.3g 6827-122 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm. 3/5-->3/17/93

FIGURE 115

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R-63 72.3g 6827-122 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm. 3/5-->3/17/93

FIGURE 116

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701R-63 72.3g 6827-122 in 290g C30 oil

H₂:CO in feed=0.7, 1100 rpm. 3/5-->3/7/93

COMPARISON OF TWO ORGANO-POTASSIUM COMPOUNDS

RUN NO.	49		63
MODE OF K ADDITION	K ₂ CO ₃ + K LAURATE IN SOLUTION		K ₂ CO ₃ + K NONYLPHENOLATE IN SOLUTION
TOTAL K, g/100 g Fe	2.4	3.0	2.3
CO CONVERSION, %	70	70	50
SELECTIVITIES			
C ₁ -C ₂	3.1	2.7	5.0
C ₂ -C ₃	1.1	0.7	2.1
C ₃ -C ₄	2.1	2.1	1.8
C ₄ -C ₅	0.7	0.6	1.0
C ₅ -C ₆	4.2	3.8	6.0
C ₆ -C ₇	0.7	0.6	1.0
C ₇ -C ₈	3.0	2.8	5.0
OLEFIN/PARAFFIN RATIO			
C ₂ -C ₃	1.9	3.0	0.9
C ₃ -C ₄	6.0	6.3	6.0
C ₄ -C ₅	4.3	4.7	5.0

FIGURE 117

FIGURE 118

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R-63 72.3g 6827-122 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm. 3/5-->3/17/93

FIGURE 119

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R-63 72.3g 6827-122 in 290g C₃₀ oil

H₂:CO in feed=0.7, 1100 rpm. 3/5-->3/17/93

FIGURE 120

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLANT 701 R-65 25g 6827-108A in 290g C₃₀ oil

H₂:CO feed = 0.7, rpm=1100, 3/27-->4/11/93

FIGURE 121

PRECIPITATED IRON CATALYST IN SLURRY AUTOVLAVE REACTOR

PLANT 701 R-65 25g 6827-108A in 290g C₃₀ oil

H₂:CO feed = 0.7, rpm=1100, 3/27-->4/11/93

FIGURE 122

PRECIPITATED IRON CATALYST IN SLURRY AUTOVLAVE REACTOR

PLANT 701 R-65 25g 6827-108A in 290g C₃₀ oil

H₂:CO feed = 0.7, rpm=1100, 3/27-->4/11/93

FIGURE 123

PRECIPITATED IRON CATALYST IN SLURRY AUTOVLAVE REACTOR

PLANT 701 R-65 25g 6827-108A in 290g C₃₀ oil

H₂:CO feed = 0.7, rpm=1100, 3/27-->4/1/93

FIGURE 124

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLANT 701 R-65 25g 6827-108A in 290g C30 oil

H₂:CO feed = 0.7, rpm=1100, 3/27-->4/11/93

**PHYSICAL PROPERTIES OF DIFFERENT MESH RANGE IRON OXIDES AND
ONE FROM IRON/COPPER OXALATE DECOMPOSITION**

Fe/Cu OXIDES	MESH RANGE	METALS, WT%			BET	
		Fe	Cu	Si	SA, m ² /g	PV, cc/g
RUN 30, DIRECT	-140 + 400	65.5	2.1	N/A	97	0.47
RUN 30, DIRECT	-400	65.9	2.1	N/A	94	0.41
Fe/Cu OXALATE DECOMPOSITION	POWDER	62.7	2.8	N/A	206	0.10

FIGURE 125

AFFECT OF MESH SIZE ON CATALYST PERFORMANCE AND PERFORMANCE OF AN EXPERIMENTAL OXALATE-DERIVED CATALYST

RUN NO.	58	59	60
MODE OF K ADDITION	SOLID K LAURATE TO RX AT STARTUP		
TOTAL K, g/100 g Fe	2.1		2.2
HOURS ON STREAM	150		
CO CONVERSION, %	20	39	39
SELECTIVITIES			
C ₂ /C ₁	1.8	2.5 [†]	2.0
C ₃ /C ₁	0.0	0.5	0.4
C ₄ /C ₁	0.7	1.1	0.8
C ₅ /C ₁	0.0	0.8	0.7
C ₆ /C ₁	2.7	3.9	3.2
C ₇ /C ₁	0.0	0.9	0.5
C ₈ /C ₁	1.7	3.0	2.2
OLEFIN/PARAFFIN RATIO			
C ₂ /C ₃	∞	2.2	2.0
C ₃ /C ₄	∞	4.9	4.6
C ₄ /C ₅	∞	3.3	4.4

1. THE SELECTIVITIES FROM RUN 59 DID NOT LINE OUT WHEN THE CONVERSIONS DID. THE

FIGURE 127

PERFORMANCE COMPARISON

○ RUN 58, THROUGH 140 ON 400 MESH.

□ RUN 59, THROUGH 400 MESH

TARGET TEMP, °C

← 280 →

265

PRESSURE, psig

← 153 →

290

FEED, NL/Hr g Fe

← 5.82 →

6.97

H₂/CO
USAGE

0.8
0.7
0.6
0.5
0.4

CO
CONVERSION

100
80
60
40
20
0

H₂
CONVERSION

100
80
60
40
20
0

CO + H₂
CONVERSION

100
80
60
40
20
0

HOURS ON STREAM

FIGURE 128

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

□ RUN 59

○ RUN 60

TARGET TEMP, °C

<280>

265

PRESSURE, psig

<153>

290

FEED, NL/Hr g Fe

<5.82>

6.97

FIGUR 129

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE 130

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE 131

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

□ RUN 59

○ RUN 60

FIGURE 132

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE 133

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

□ RUN 59

○ RUN 60

TARGET TEMP, °C

<280>

265

PRESSURE, psig

<153>

290

FEED, NL/Hr g Fe

<5.82>

6.97

FIGURE 134

COMPARISON OF RUNS 59 & 60 ; PLANT 701 AUTOCLAVE

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE 135

CO ACTIVATION OF Fe/Cu OXIDE

PLANT 701 R-71 72.3g 6827-165B in 290g C₃₀ oil

H₂:CO feed = 0.7, 1100 rpm, 7/14--->7/18/93

FIGURE 136

CO ACTIVATION OF Fe/Cu OXIDE

PLANT 701 R-71 72.3g 6827-165B in 290g C₃₀ oil

H₂:CO feed = 0.7, 1100 rpm, 7/14--->7/18/93

FIGURE 137

CO ACTIVATION OF Fe/Cu OXIDE

PLANT 701 R-71 72.3g 6B27-165B in 290g C₃₀ oil

H₂:CO feed = 0.7, 1100 rpm, 7/14--->7/18/93

FIGURE 138

CO ACTIVATION OF Fe/Cu OXIDE
 PLANT 701 R-71 72.3g 6827-165B in 290g C₃₀ oil
 H₂:CO feed = 0.7, 1100 rpm, 7/14--->7/18/93

FIGURE 139

CO ACTIVATION OF Fe/Cu OXIDE
 PLANT 701 R-71 72.3g 6B27-165B in 290g C₃₀ oil
 H₂:CO feed = 0.7, 1100 rpm, 7/14---->7/18/93

FIGURE 140

CO ACTIVATION OF K-FREE Fe/Cu OXIDE

PLANT 701 R-72 72.3g 6827-165B in 290g C₃₀ oil

H₂:CO feed = 0.7, 1100 rpm, 7/28---->8/25/93

THE TWO CARBON MONOXIDE ACTIVATED CATALYSTS:

PERFORMANCE COMPARISON

RUN NO.	71	72	
MODE OF K ADDITION	SOLID K LAURATE	K LAURATE IN SOLUTION	
TOTAL K, g/100 g Fe	2.4	0.0	2.1
HOURS ON STREAM	95	95	650
CO CONVERSION, %	90	90	82
SELECTIVITIES			
C ₂ /C ₁	7.0	10.0	6.5
C ₃ /C ₁	5.5	9.0	4.5
C ₄ /C ₁	2.6	1.5	3.0
C ₅ /C ₁	2.3	5.0	2.0
C ₆ /C ₁	8.7	9.0	10.0
C ₇ /C ₁	N/A	0.0	0.0
C ₈ /C ₁	N/A	7.5	6.5
OLEFIN/PARAFFIN RATIO			
C ₂ /C ₁	0.47	0.17	0.67
C ₃ /C ₁	3.8	1.8	5.0
C ₄ /C ₁	N/A	∞	∞

FIGURE 141

FIGURE 142

CO ACTIVATION OF K-FREE Fe/Cu OXIDE

PLANT 701 R-72 72.3g 6827-165B in 290g C₃₀ oil

H₂:CO feed = 0.7, 1100 rpm, 7/28--->8/25/93

FIGURE 143

CO ACTIVATION OF K-FREE Fe/Cu OXIDE

PLANT 701 R-72 72.3g 6827-165B in 290g C₃₀ oil

H₂:CO feed = 0.7, 1100 rpm, 7/28--->8/25/93

FIGURE 144
CO ACTIVATION OF K-FREE Fe/Cu OXIDE
 PLANT 701 R-72 72.3g 6827-165B in 290g C₃₀ oil
 H₂:CO feed = 0.7, 1100 rpm, 7/28---->8/25/93

FIGURE 145
CO ACTIVATION OF K-FREE Fe/Cu OXIDE
 PLANT 701 R-72 72.3g 6827-165B in 290g C₃₀ oil
 H₂:CO feed = 0.7, 1100 rpm, 7/28---->8/25/93

FIGURE 146
CO ACTIVATION OF K-FREE Fe/Cu OXIDE
 PLANT 701 R-72 72.3g 6827-165B In 290g C₃₀ oil
 H₂:CO feed = 0.7, 1100 rpm, 7/28--->8/25/93

UCI CATALYST
PHYSICAL PROPERTIES

SOURCE OF CATALYST	METALS, WT %, V.F.				Fe:K (WT)	BET	
	Fe	Cu	Si	K		SA, m ² /g	PV, cc/g
UNITED CATALYSTS (UCD)	54.9	4.01	5.3	3.7	100 : 6.7	95	0.28

FIGURE 147

LAPORTE TEST CATALYST IN STIRRED AUTOCLAVE

72.7g 6827-62 in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE 149

LaPORTE TEST CATALYST IN STIRRED AUTOCLAVE

72.7g 6827-62 in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE 150
LaPORTE TEST CATALYST IN STIRRED AUTOCLAVE
 72.7g 6827-62 in 290g C₃₀ oil
 H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE 151
LaPORTE TEST CATALYST IN STIRRED AUTOCLAVE
 72.7g 6827-62 in 290g C₃₀ oil
 H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE 152 **LaPORTE TEST CATALYST IN STIRRED AUTOCLAVE**

72.7g 6827-62 in 290g C₃₀ oil

H₂:CO in feed = 0.7, stirrer rpm = 1100

FIGURE 153

CATALYSTS FROM VARIOUS SOURCES OF POTASSIUM
MEDIUM AND HIGH POTASSIUM LEVELS

⊙ • KL @ START, 255° C AND 265° C, 2.1 K

□ KL @ START, 265° C, NORMAL AND 1/2 NORMAL FEED RATE, 3.6 K

× KC IMPREG, 265° C, 2.1 K

⊗ KL DURING RUN, 265° C, 2.5 K

⊗ KC IMPREG, 265° C, 3.9 K

⊗ KL DURING RUN, 265° C AND UP, 3.6 K

□ KC IMPREG + KL DURING RUN, 265° C, 2.4 K

⊙ KC IMPREG + KL DURING RUN, 265° C, 3.0 K

FIGURE 154

**CATALYSTS FROM VARIOUS SOURCES OF POTASSIUM
MEDIUM AND HIGH POTASSIUM LEVELS**

⊙ • KL @ START, 255° C AND 265° C, 2.1 K

◻ KL @ START, 265° C, NORMAL AND 1/2 NORMAL FEED RATE, 3.6 K

× KC IMPREG, 265° C, 2.1 K

⌘ KL DURING RUN, 265° C, 2.5 K

⊗ KC IMPREG, 265° C, 3.9 K

⊞ KL DURING RUN, 265° C AND UP, 3.6 K

◻ KC IMPREG + KL DURING RUN, 265° C, 2.4 K

⊞ KC IMPREG + KL DURING RUN, 265° C, 3.0 K

FIGURE 155

**CATALYSTS FROM VARIOUS SOURCES OF POTASSIUM
MEDIUM AND HIGH POTASSIUM LEVELS**

⊙ • KL @ START, 255° C AND 265° C, 2.1 K

◻ KL @ START, 265° C, NORMAL AND 1/2 NORMAL FEED RATE, 3.6 K

× KC IMPREG, 265° C, 2.1 K

⌘ KL DURING RUN, 265° C, 2.5 K

⊗ KC IMPREG, 265° C, 3.9 K

⊗ KL DURING RUN, 265° C AND UP, 3.6 K

◻ KC IMPREG + KL DURING RUN, 265° C, 2.4 K

⊙ KC IMPREG + KL DURING RUN, 265° C, 3.0 K

FIGURE 156

**CATALYSTS FROM VARIOUS SOURCES OF POTASSIUM
MEDIUM AND HIGH POTASSIUM LEVELS**

⊙ • KL @ START, 255° C AND 265° C, 2.1 K

◻ ◻ KL @ START, 265° C, NORMAL AND 1/2 NORMAL FEED RATE, 3.6 K

× KC IMPREG, 265° C, 2.1 K

⌘ KL DURING RUN, 265° C, 2.5 K

⊗ KC IMPREG, 265° C, 3.9 K

⊗ KL DURING RUN, 265° C AND UP, 3.6 K

◻ KC IMPREG + KL DURING RUN, 265° C, 2.4 K

⊕ KC IMPREG + KL DURING RUN, 265° C, 3.0 K

FIGURE 157

**CATALYSTS FROM VARIOUS SOURCES OF POTASSIUM
MEDIUM AND HIGH POTASSIUM LEVELS**

⊙ • KL @ START, 255° C AND 265° C, 2.1 K

◻ KL @ START, 265° C, NORMAL AND 1/2 NORMAL FEED RATE, 3.6 K

× KC IMPREG, 265° C, 2.1 K

⌘ KL DURING RUN, 265° C, 2.5 K

⊗ KC IMPREG, 265° C, 3.9 K

⊗ KL DURING RUN, 265° C AND UP, 3.6 K

◻ KC IMPREG + KL DURING RUN, 265° C, 2.4 K

⊕ KC IMPREG + KL DURING RUN, 265° C, 3.0 K

FIGURE 158

**CATALYSTS FROM VARIOUS SOURCES OF POTASSIUM
MEDIUM AND HIGH POTASSIUM LEVELS**

⊙ • KL @ START, 255° C AND 265° C, 2.1 K

◻ KL @ START, 265° C, NORMAL AND 1/2 NORMAL FEED RATE, 3.6 K

× KC IMPREG, 265° C, 2.1 K

⊠ KL DURING RUN, 265° C, 2.5 K

⊗ KC IMPREG, 265° C, 3.9 K

⊞ KL DURING RUN, 265° C AND UP, 3.6 K

◻ KC IMPREG + KL DURING RUN, 265° C, 2.4 K

◻ KC IMPREG + KL DURING RUN, 265° C, 3.0 K

FIGURE 159

CATALYSTS FROM VARIOUS SOURCES OF POTASSIUM
MEDIUM AND HIGH POTASSIUM LEVELS

⊙ • KL @ START, 255° C AND 265° C, 2.1 K

◻ KL @ START, 265° C, NORMAL AND 1/2 NORMAL FEED RATE, 3.6 K

× KC IMPREG, 265° C, 2.1 K

⌘ KL DURING RUN, 265° C, 2.5 K

⊗ KC IMPREG, 265° C, 3.9 K

⊗ KL DURING RUN, 265° C AND UP, 3.6 K

◻ KC IMPREG + KL DURING RUN, 265° C, 2.4 K

⊗ KC IMPREG + KL DURING RUN, 265° C, 3.0 K

FIGURE 160

COMPARISON OF CARBON MONOXIDE ACTIVATION
TO
SYNTHESIS GAS ACTIVATION

⊙ CO ACTIVATION, KL @ START, 265° C, 2.4 K

FIGURE 161

COMPARISON OF CARBON MONOXIDE ACTIVATION
TO
SYNTHESIS GAS ACTIVATION

⊙ CO ACTIVATION, KL @ START, 265° C, 2.4 K

FIGURE 162

**COMPARISON OF CARBON MONOXIDE ACTIVATION
TO
SYNTHESIS GAS ACTIVATION**

⊗ CO ACTIVATION, KL @ START, 265° C, 2.4 K

FIGURE 163

COMPARISON OF CARBON MONOXIDE ACTIVATION TO SYNTHESIS GAS ACTIVATION

⊙ CO ACTIVATION, KL @ START, 265° C, 2.4 K

FIGURE 164

**COMPARISON OF CARBON MONOXIDE ACTIVATION
TO
SYNTHESIS GAS ACTIVATION**

⊙ CO ACTIVATION, KL @ START, 265° C, 2.4 K

CONVERSION AND SELECTIVITY CALCULATIONS

CALCULATIONS USE ON LINE GAS ANALYSES

C = CONCENTRATION IN MOLE %

CONVERSIONS

$$\text{CONVERSION (CO)} = \frac{\left(\frac{C_{CO}}{C_{Ar}}\right)_{\text{Feed}} - \left(\frac{C_{CO}}{C_{Ar}}\right)_{\text{Prod}}}{\left(\frac{C_{CO}}{C_{Ar}}\right)_{\text{Feed}}}$$

$$\text{CONVERSION (H}_2\text{)} = \frac{\left(\frac{C_{H_2}}{C_{Ar}}\right)_{\text{Feed}} - \left(\frac{C_{H_2}}{C_{Ar}}\right)_{\text{Prod}}}{\left(\frac{C_{H_2}}{C_{Ar}}\right)_{\text{Feed}}}$$

$$\text{CONVERSION (CO + H}_2\text{)} = \frac{\left(\frac{C_{CO} + C_{H_2}}{C_{Ar}}\right)_{\text{Feed}} - \left(\frac{C_{CO} + C_{H_2}}{C_{Ar}}\right)_{\text{Prod}}}{\left(\frac{C_{CO} + C_{H_2}}{C_{Ar}}\right)_{\text{Feed}}}$$

SELECTIVITIES

$$S_n = \frac{\left(\frac{C_n}{C_{Ar}}\right)_{Prod}}{\left(\frac{C_{Co}}{C_{Ar}}\right)_{Feed} - \left(\frac{C_{Co}}{C_{Ar}}\right)_{Prod}}$$

The equation above yields carbon-based selectivities. Before being used the selectivities were corrected for carbon dioxide formation in all cases except for that of carbon dioxide itself. Since carbon dioxide selectivities were usually about 50%, the corrected selectivities were about twice as high as they would have been if the carbon going to carbon dioxide had been taken into account in their calculation.

CALCULATION OF CONTACT TIME

$\bar{V}$ is Volume of liquid in Autoclave

W is weight in grams of non

material balance:

$$F_0 - F = \bar{r} \cdot W \cdot \bar{V}$$

$$F_0 - F_0(1-x) = \bar{r} \cdot W \cdot \bar{V}$$

$$F_0 x = \bar{r} \cdot W \cdot \bar{V}$$

$$\bar{r} = \frac{F_0 x}{W \bar{V}} = \frac{x}{\left(\frac{W \bar{V}}{F_0} \right)}$$

$$\frac{W \bar{V}}{F_0} = \text{CONTACT TIME (space time)}$$

APPENDIX 2

NONLINEAR REGRESSION OF THE FISCHER-TROPSCH PRODUCT DISTRIBUTION BY A DOUBLE α MODEL

THE SINGLE α MODEL

Classical Shulz-Flory theory states that the hydrocarbon product of the Fischer-Tropsch process can be described by the equation:

$$M_n = (1-\alpha) \alpha^{(n-1)} \quad (1)$$

where M_n is the mole fraction of the product of carbon number n , and α is the chain growth probability, defined as

$$\alpha = \frac{r_p}{r_p + r_t} \quad (2)$$

where r_p and r_t are the rate of propagation and termination, respectively.

Equation (1) is called a single α model since it describes the product distribution over the entire range of carbon number by a single parameter α . From Equation (1) one gets

$$\ln(M_n) = n \ln \alpha + \ln \frac{1-\alpha}{\alpha} \quad (3)$$

Equation (3) tells that this single α model generates a straight line in a $\ln(M_n) - n$ plot, and the slope of the line will be the log of α .

DEVELOPMENT OF DOUBLE α MODELS

The single α model has been successfully applied to, for example, the product on a fused iron catalyst (Satterfield and Huff, 1982). However, a break point was observed in many cases which separates the distribution into two regions. This phenomenon was first found in 1943 by tests conducted in Germany, and more and more similar cases were reported since then (Huff and Satterfield, 1984; Donnelly et al, 1988). As a consequence, the single α model has been modified to account for the two region distributions. The simplest way to do this is using the single α model in each region and thus two straight lines result, each giving an α for the specific region (Huff and Satterfield, 1984; Madon and Teylon, 1981). Based on experimental observations, Huff (Huff, 1982) proposed a two-site theory, which assumes that two kinds of sites on the surface of the catalyst exist, one in favor of producing lighter products and the other heavier products. When the products produced at these two kinds of sites do not interact, and assume that x percent of the total moles of the products are produced at site 1, the total product is then the sum of products from the two sites:

$$M_n = x(1-\alpha_1)\alpha_1^{n-1} + (1-x)(1-\alpha_2)\alpha_2^{n-1} \quad (4)$$

Equation (4) contains three parameters. In addition to x , α_1 and α_2 are the chain growth probabilities at the two sites, respectively. Unlike the regional fitting by the single α model, this model actually presents a continuous, smoothly changing curve in a $\ln(M_n)$ - n plot. This is better than the two separated straight lines because in many cases the two regions are not very well separated at a specific carbon number, instead, there is usually a transient region over several carbon numbers, and therefore the double α model of Equation (4) can use more data points and fit the data better (Bukur et al, 1990). When the number of the data available for evaluation of α_1 by linear (single α) model is limited, this nonlinear feature of the double α model becomes an important advantage. For this reason, the fitting of the model to the experimental data can be termed nonlinear regression.

The two-site theory is basically a pure hypothesis, and it seems difficult to argue that only two kinds of sites exist. Stenger (Stenger, 1985) tried to attack the problem by making a more realistic assumption that the chain growth probability α changes continuously over the range of carbon numbers. Based on the idea, Stenger proposed a distributed-site model. He assumed that α is a function of the local potassium concentration c , and c obeys the normal distribution. Stenger's model is also a three-parameter model and he showed that the distributed- α model and the

two-site model fit experimental data equally well, but the calculation procedure is more involved with the former because numerical integration is required. The differences between the two models are also discussed by Inoue et al (Inoue et al, 1987).

Recently Donnelly et al (Donnelly et al, 1988) proposed a double α model in the form

$$M_n = A\alpha_1^{n-1} + B\alpha_2^{n-1} \quad (5)$$

The two parameters A and B are functions of the two α 's and a third variable called the "break point" ξ , which is the carbon number at which the curve turns. The expressions of A and B can be found as follows. At the break point $n=\xi$, the contributions from each term in Equation (5) are equal, therefore we have

$$A\alpha_1^{\xi-1} = B\alpha_2^{\xi-1}$$

or

$$B = \left(\frac{\alpha_1}{\alpha_2}\right)^{\xi-1} A \quad (6)$$

A second relation between A and B can be derived by noticing that the sum of the mole fraction of all carbon numbers is unity:

$$\sum_{n=1}^{\infty} M_n = \sum_{n=1}^{\infty} (A\alpha_1^{n-1} + B\alpha_2^{n-1}) = 1 \quad (7)$$

Using the sum of the geometric series

$$\sum_{n=1}^{\infty} y^{n-1} = \frac{1}{1-y}$$

we get from Equation (7)

$$\frac{A}{1-\alpha_1} + \frac{B}{1-\alpha_2} = 1 \quad (8)$$

Equations (6) and (8) are linearly independent and can be used to evaluate A and B explicitly when the parameters α_1 , α_2 and ξ are chosen. Therefore the model given by Equation (5) is also a three parameter model which is similar to Huff's (Huff, 1982). Actually, if Equation (5) is compared with Equation (4), it can be seen that the two equations are identical if we set

$$A = x(1-\alpha_1)$$

and

$$B = (1-x)(1-\alpha_2)$$

and the break point ξ plays a similar role as x . However, Donnelly et al emphasize that the model given by Equation (5) is not based on any theoretical assumptions about the cause of the double α phenomenon, instead, it is a mathematical tool to provide a tractable measure of evaluating α 's by fitting the experimental data. The nonlinear regression method associated with this model is by choosing α_1 , α_2 and ξ to minimize the sum of the squared errors:

$$\phi = \sum_{n=1}^k [\ln(M_n) - \ln(m_n)]^2 \quad (9)$$

where M_n is calculated mole fraction of product of carbon number n by Equation (5), and m_n is actually measured mole fraction. The sum is taken from 1 to k , with k being the highest carbon number where reliable data are available.

MODELS USING WEIGHT FRACTIONS

In many cases the product distribution is more conveniently expressed by weight fraction rather than the mole fraction. Assume that during the chain growth, the molecular weight of each additional carbon unit is the same, the single α model corresponding to Equation (1) is given as (Satterfield et al,

1982):

$$W_n = n(1-\alpha)^2 \alpha^{n-1} \quad (10)$$

where W_n is the weight fraction of the product of carbon number n . Similarly to the development of the double α model of Equation (5) we propose a weight fraction distribution:

$$\frac{W_n}{n} = C_1 \alpha_1^{n-1} + C_2 \alpha_2^{n-1} \quad (11)$$

The two relations giving C_1 and C_2 are given, in this case, by

$$C_2 = \left(\frac{\alpha_1}{\alpha_2} \right)^{t-1} C_1 \quad (12)$$

and

$$\sum_{n=1}^{\infty} W_n = \sum_{n=1}^{\infty} (C_1 n \alpha_1^{n-1} + C_2 n \alpha_2^{n-1}) = 1 \quad (13)$$

The binomial series relation gives

$$\sum_{n=1}^{\infty} n y^{n-1} = \frac{1}{(1-y)^2}$$

Therefore the second relation between C_1 and C_2 is

$$\frac{C_1}{(1-\alpha_1)^2} + \frac{C_2}{(1-\alpha_2)^2} = 1 \quad (14)$$

The nonlinear regression is done by choosing α_1 , α_2 and ξ to minimize the sum of the squared errors:

$$\Delta = \sum_{n=1}^k [\ln(W_n) - \ln(w_n)]^2$$

where W_n and w_n are the weight fractions calculated from Equation (11) and from the experimental data, respectively.

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APPENDIX 3

Date: 3 NOV 93

From: Alan E. van Til & Ronald S. Smyczynski

To: George J. Antos

Subject: Fischer-Tropsch (10834-0016), #17

This month, three additional TGA carbide synthesis runs were made since the last report to you. We first heated ca. 200 mg of material to nominally 200 °C in a 1-torr vacuum to remove the two waters of hydration from the K,Cu,Fe oxalate. Then, the material was further heated to 250 °C in H₂ at atmospheric pressure to remove the remaining carbonaceous species and form doped Fe(O). The temperature was purposely kept below or near 300 °C to avoid sintering since all previous work via TGA and scaleup showed loss of surface area above 300 °C. Although it may not be necessary in commercial practice of this synthetic pathway, we wanted to bring the doped Fe catalyst to a definite thermodynamic starting point, that of full reduction to Fe(O) before cutting in CO or CO/H₂; therefore, we normally used H₂ to fully reduce the iron. The first run made this month, RUN #14, also used 2:1 H₂:CO as was done earlier in RUN's 7-12. The second run, #15, had to be aborted due to the thermalbalance lifting mechanism jamming. Three weeks later after finally finding the true problem, we finally finished this series with RUN #16, where the H₂:CO ratio was set nominally at 1. The thermalbalance, a Mettler TA-2 is 22 years old, therefore, Mettler does not support it with spare parts any longer. Also, the level of repair done by us here of total disassembly was originally done under service contract and accordingly we have no manuals explaining how to do such work. The primary results from the present runs are that increased H₂ improves CO conversion dramatically and after about 10 HOS produces more wax as seen in Figure 1. In contrast of earlier runs carried out at 300 °C, the wax formation on the sample & sample stick continued with little change for 100+ hrs. Samples of the product gases were taken in RUN's 14 & 16. The results are not consistent throughout as we would like because of sampling problems inherent to the use of sample tubes. However, they do provide very useful information. Namely, at 250 °C in contrast to the earlier results of RUN #11 at 300 °C, with 2:1 H₂:CO, we are producing C₂ & C₃'s. We would not know that fact without gas analysis. Also, CO₂ is being produced throughout RUN #14 but not in RUN #16 where it stopped after 20+ hrs. Little or no methane was produced over this catalyst at 250 °C when the H₂:CO ratio=1. In summary, from our work using a thermalbalance microreactor for F-T and butene isomerization, we suggest that a GC be found to hook to analyze product gases on-line to produce more consistent results. Finally, the techniques shown here where the catalyst mass is continuously monitored should provide the means of evaluating ideas on how to reduce wax buildup which fundamentally limits catalyst performance. Much shorter run times of about 24-hrs should be sufficient for this purpose.

Figures 2-6 summarize our microreactor run data. The bulk thermoanalytical data for each run are given in Table 1. Table 2 lists our gas sample results taken during RUN #11. Using the usual method of calculating conversions from the mole ratio of species to N_2 , we obtain Table 3. Similarly, Tables 4-7 list the present gas analysis results for RUN's 14 & 16. From the data accumulated to date, the recommended procedure for scaleup of our F-T iron carbide catalyst is as follows:

- (1) Use a stirred autoclave without supporting liquid.
- (2) Heat doped iron oxalate to 200 °C while stirring slowly under rotary pump vacuum at 1-2 torr collecting water evolved in trap(s). Continue heating until no more water is evolved and as a check that water collected mass balances with the two waters of hydration.
- (3) Bring autoclave back to atmospheric pressure with N_2 , then cut in H_2 and heat to 250 °C. Use a CO or CO_2 monitor connected to the autoclave outlet to tell when we have removed the initial carbonaceous species from the iron. Continue heating until we reach near zero lineout, and then cut in CO and raise pressure to about 50 psig. Hold temperature for 6-8 hrs and finally cool down under $H_2 + CO$ to RT. Cut reaction gases and sparge with N_2 . Finally, cut pressure and stirring.

REFERENCES: (1) UOP RESEARCH REPORT 42-3-17U, A.E. van Til,
March, 1993
(2) UOP B# 6753:126,128,130

CC: SABRADLEY, RFRAME, MJCOHN, TMMEZZA

TABLE 1
THERMOANALYTICAL DATA FOR DOPED Fe₂Cy FROM Fe,Cu,K OXALATE
BY VACUUM, H₂, AND CO OR CO/H₂ TREATMENT AT 250 or 300 °C

<u>RUN #</u>	<u>ms.i (mg)</u> <u>(a.b.)</u>	<u>ms.f (mg)</u> <u>(a.b.)</u>	<u>% Mass</u> <u>Loss</u> <u>(a.b.)</u>	<u>% Mass</u> <u>Loss</u> <u>(t.b.)</u>	<u>Rx</u> <u>Gas</u> <u>P (psia)</u>	<u>BET</u> <u>S.A.</u> <u>(m²/g)</u>
1 CO	218.05	95.73	56.10	61.84	CO (14.7)	
2	202.07	81.68	59.58	59.95	CO (14.7)	
3	199.86	82.54	58.70	60.95	CO (14.7)	37
4	201.90	142.64	29.35	34.35	CO (65)	
5	206.12	75.75	63.63	61.93	CO/H ₂ =1 (14.7)	13
6	202.91	87.39	56.93	59.93	CO/H ₂ =1 (65)	52
7	202.03	94.97	52.99	53.85	CO/H ₂ =2 (65)	19
8	209.79	117.61	43.94	38.97	CO/H ₂ =2 (65)	
9	212.26	110.11	48.12	41.16	CO/H ₂ =2 (65)	
10 VAC	202.50	124.94	38.30	29.58	CO/H ₂ =2 (65)	
11	202.58	126.00	37.80	28.02	CO/H ₂ =2 (65)	
12 250°C	199.36	128.89	35.35	25.63	CO/H ₂ =2 (65)	
13	200.28	82.26	58.93	59.27	CO/H ₂ =2 (14.7, 65)	
14 250°C	206.34	157.42	23.71	0.77	CO/H ₂ =2 (65)	
15	204.67	RUN	ABORTED			
16 250°C	208.44	160.29	23.10	4.75	CO/H ₂ =1 (65)	

- NOTES: 1) RUN #1 prep and carbiding done entirely in CO after vacuum treatment at 1-torr up to and holding to mass lineout at 200 °C. Balance was backfilled with UHP N₂ before cutting in CO over the sample.
- 2) RUN #10 sample prep done entirely in vacuum to 300 °C rather than stopping at 200 °C, backfilling with UHP N₂ to atmospheric pressure and cutting in H₂ over the sample and continuing the heating to 300 °C (RUN's 2-9).
- 3) RUN #11 was a repeat of RUN's 7-9 conditions and gas samples were also taken.
- 4) RUN #12 prep was done using H₂ sweep at 250 °C. After mass lineout, CO was cut in and the temperature was held at 250 °C for 84+hrs.
- 5) RUN #14, Total HOS with CO=94.5
- 6) RUN #16, Total HOS with CO=117

TABLE 2

GAS SAMPLE RESULTS FROM RUN #11. TGA F-T CARRIDE SYNTHESIS

TIME (HOS)	CO Mol %	CO ₂ Mol %	H ₂ Mol %	CH ₄ Mol %	N ₂ Mol %
0.25	3.5	1.0	35.1		59.7
6.0	9.5	0.6	26.4	0.2	62.5
24.0	12.4	0.3	29.8	0.3	56.7
31.0	10.3	0.1	24.6	0.2	64.4
49.5 Reactor Cooled	12.2		31.4		56.1

TABLE 3

CONVERSION AND SELECTIVITY DATA FOR RUN #11 FROM GC ANALYSIS

TIME HOS	CO Percent Conversion	H ₂ /CO	CO ₂ Percent Selectivity	CH ₄ Percent Selectivity
0.25	73.0	10.0	10.5	
6.0	30.1	2.78	14.7	4.9
24.0		2.40		
31.0	26.5	2.36	2.7	5.6

TABLE 4

GAS SAMPLE RESULTS FROM RUN #14. TGA F-T CARBIDE SYNTHESIS

TIME (HOS)	CO Mol %	CO ₂ Mol %	H ₂ Mol %	CH ₄ Mol %	SUM(C ₂ +C ₃) Mol %	N ₂ Mol %
0.25	1.5	0.4	8.2			89.5
4	4.6	0.7	19.0	0.1		75.1
12	17.0	3.3	47.6	0.6	0.4	30.6
20	10.0	1.7	22.5	0.4	0.1	54.4
30	10.1	1.0	32.4	0.2		56.2
40	11.8	1.4	35.6	0.3	0.2	50.5
50	13.0	1.0	38.8	0.2		46.9
72	9.2	1.0	29.9	0.2		59.6
94.25	10.1	1.0	32.0	0.2		56.6
After Cool Down	12.0	0.1	31.5			56.3

TABLE 5

CONVERSION AND SELECTIVITY DATA FOR RUN #14 FROM GC ANALYSIS

TIME (HOS)	CO % Conv.	H ₂ /CO	CO ₂ % Sel.	CH ₄ % Sel.	C ₂ +C ₃ % Sel.
0.25	92.1	5.44	2.3		
4	71.3	4.12	6.1	0.9	
12		2.8			
20	13.8	2.25	107	25	6.3
30	15.7	3.21	53	11	
40		3.03			
50		2.99			
72	27.6	3.25	29	5.7	
94.25	16.3	3.17	51	10	

TABLE 6

GAS SAMPLE RESULTS FROM RUN #16. TGA F-T CARBIDE SYNTHESIS

TIME (HOS)	CO Mol %	CO ₂ Mol %	H ₂ Mol %	N ₂ Mol %
0.25	2.6	0.1	4.0	93.0
4	4.2	0.2	6.5	88.8
12	8.5	0.2	11.9	79.0
20	9.5	0.2	13.6	76.4
30	Sampling	Problem		
40	0.1		1.0	79.5
50	8.3		11.7	79.6
72	Sampling	Problem		
94.25	7.8		11.2	80.7
116.75	7.7		11.1	80.8
After Cooldown	7.8		11.3	80.6

TABLE 7

CONVERSION AND SELECTIVITY DATA FOR RUN #16 FROM GC ANALYSIS

TIME (HOS)	CO % Conversion	H ₂ /CO	CO ₂ % Selectivity
0.25	71.1	1.54	1.6
4	51.1	1.55	4.6
12		1.40	
20		1.43	
30			
40			
50		1.41	
72			
94.25	0.1	1.43	
116.75	1.5	1.44	
After Cooldown		1.45	

TGA Prep: Fe,Cu,K Carbide from Oxalate

SN# E753-66, Is.w.=0.08 g, P=50 psig

TGA Prep: Fe,Cu,K Carbide from Oxalate

SP# 6753-66, 1.541=0.20634 g

TGA Prep: Fe,Cu,K Carbide from Oxalate

SP 67531-06, 13.47, 0.22534 g

TGA Prep: Fe,Cu,K Carbide from Oxalate

SW 5753-66, 13.0000 g, P=500 psig

Time (hr)
 --- RUN #14, 12.00 = 2

TGA Prep: Fe₂Cu₂H Carbide from Oxalate

SW 4753-05 10.0.00\20944.g

TGA Prep: Fe,Cu,K Carbide from Oxalate

SA: F753-68, Wt. = 0.00337 g, P = 90 g/mg

APPENDIX 4

Lewis Liu used the data set below from Run 43, Plant 700B (or 701) to calculate a rate constant. Run 43 was the second run with potassium laurate. He used a rate expression based on earlier literature work, references to which are attached. The data set is on the following pages:

Hours on Stream	Feed Rate $Q_{\text{Co}+\text{H}_2}$	$(Q_{\text{Co}+\text{H}_2})^{-1}$	$x_{\text{H}_2}^2$	V^3	$F(x_{\text{H}_2})^4$
15-152	24	.417	55	.56	.846
152-220	1.2	.833	70	.57	1.419
222-240	3.8	.263	43	.58	.573
240-246	5.2	.192	31	.61	.371
246-296	1.2	.833	73	.58	1.598
296-326	6.7	.149	29	.57	.342

1. NL/hr. g Fe

2. Conversion

3. H_2/Co Usage Ratio

4. $f(x_{\text{H}_2})$ from the following:

$$\frac{(1 + \frac{1}{U}) x_{\text{H}_2} (1 + \alpha^* x_{\text{H}_2})}{1 - x_{\text{H}_2}} = Da$$

$$\alpha^* = \alpha \frac{1 + \frac{1}{U}}{1 + \frac{1}{F}} = \alpha \frac{1 + \frac{1}{U}}{1 + \frac{1}{.7}} \Rightarrow F = \text{Feed Ratio} = 0.7 \quad (\text{H}_2 : \text{Co ratio})$$

$$\text{Let } \alpha = -0.5 \quad U \approx .578 \therefore \alpha^* = -\underline{.56}$$

$$\text{Let } \frac{(1 - 0.56 x_{\text{H}_2}) x_{\text{H}_2}}{1 - x_{\text{H}_2}} = f(x_{\text{H}_2})$$

(α is gas volume reduction due to conversion)

$$D_a = \frac{K M_{cat} RT}{H_{H_2} Q_{CoTH_2}}$$

K = This is a constant (Reaction Rate Parameter) if the reaction is first order in dissolved hydrogen.
Reaction is usually first order in H_2 .

M_{cat} = mass of iron

CSTR MODEL OF SLURRY REACTORS FOR FISCHER-TROPSCH SYNTHESIS

STOICHIOMETRY (Ledakowicz, et al, 1985)

Fischer-Tropsch

Water Gas Shift (WGS)

Overall Reaction

Where $z = \text{C}_m\text{H}_{2m}$ produced by reaction (1), mole;

$y = \text{H}_2\text{O}$ produced by WGS, mole.

SELECTION OF A KINETIC MODEL

Available Kinetic Models

Deckwer et al (1986) have given a good summary of the kinetic models of the Fischer-Tropsch Synthesis (FTS) in the slurry phase. The common features of these models are:

(1) The conversion rate of H_2CO is directly proportional to the hydrogen concentration in the slurry;

(2) The effect of CO is considered.

The main difference is which of the inhibition effects by CO , or H_2O is included.

$(\text{CO}_2?)$

Accordingly, they can be summarized into three groups:

(A) "H₂O only". This model was proposed by Satterfield and co-workers and verified by experimental data with reduced fused magnetite catalyst (Huff and Satterfield, 1984a; Yates and Satterfield, 1989). Using a method of deliberate addition of H₂O in the synthesis gas feed, Deckwer et al (1986) also confirmed the correlation. This model is given as (Deckwer et al, 1986):

$$-r_{CO, H_2} = \frac{b_1 C_{H_2}}{1 + b_2 (C_{H_2} O / C_{H_2} C_{CO})} \quad (4)$$

This model considers the inhibition of the reaction rate due to the competitive chemisorption of the H₂O on the catalyst surface. This is valid when a less strong WGS promoting catalyst is used and the CO conversion is high, because under such conditions the product will contain relatively large portion of water and its effect may become predominant.

(B) "CO₂ only". This model was proposed by Deckwer and co-workers and verified by experimental data with Potassium-promoted Iron catalyst (Ledakowicz et al, 1985; Deckwer et al, 1986). This model is given as (Deckwer et al, 1986):

$$-r_{CO, H_2} = \frac{b_1 C_{H_2}}{1 + b_2 (C_{CO_2} / C_{CO})} \quad (5)$$

This model includes the rate inhibition by the chemisorption of CO₂. This is the case when a highly WGS promoting catalyst is used and the CO conversion is low, because in this case the water produced by the F-T reaction is converted

probably means
"high"

almost completely to CO_2 and the effect of this product is increased.

(C) " H_2O plus CO_2 ". Considering that different kinetics may be caused by the relative importance of H_2O and CO_2 in the product, as indicated above, it is a nature extension that some investigators tried to propose a "more complete" kinetic law which includes the inhibition effect by both H_2O and CO_2 (Ledakowicz et al, 1985; Nettelhoff et al, 1985). Unfortunately, the verification of this law is unsatisfactory (Deckwer et al, 1986). The form of this law is

$$-r_{\text{CO-H}_2} = \frac{b_1 C_{\text{H}_2}}{1 + b_2 (C_{\text{CO}_2}/C_{\text{CO}}) + b_3 (C_{\text{H}_2\text{O}}/C_{\text{CO}})} \quad (6)$$

A modified form of this model was used by Yates and Satterfield (1989) to correlate experimental data and the results are still not encouraging. The correlation they used is

$$-r_{\text{CO-H}_2} = \frac{b_1 C_{\text{H}_2}}{1 + b_2 (C_{\text{CO}_2}/C_{\text{CO}}) + b_3 (C_{\text{H}_2\text{O}}/C_{\text{CO}} C_{\text{H}_2})} \quad (7)$$

Finally, it should be pointed out that in some cases, a simple first order reaction rate is possible, which can be treated as a simplified case of Equation (4) when the inhibition term of water is neglected:

$$-r_{\text{CO-H}_2} = b_1 C_{\text{H}_2} \quad (8)$$

This may be the case when CO conversion is low and the H_2/CO inlet ratio is low (Huff and Satterfield, 1984).

From the above discussions we know that which kinetic model should be used depends on the catalyst type, the operation conditions such as H_2/CO inlet ratio and conversions, and can only be determined by a test using ones own experimental data.

Test of Kinetic Models

One convenient way to test a kinetic model using experimental data is to plot the data in a proper form so one can see if the data correlates the variables in the way the model suggests. For example, Equation (4) can be rearranged in the form

$$\frac{C_{H_2}}{-r_{CO-H_2}} = \frac{1}{b_1} + \frac{b_2}{b_1} \frac{C_{H_2O}}{C_{CO}C_{H_2}} \quad (9)$$

Since the parameters b_1 and b_2 depend on in general the catalyst used and temperature, therefore if data with the same catalyst and temperature falls on a straight line in a $C_{H_2}/(-r_{CO-H_2})$ vs. $C_{H_2O}/(C_{CO}C_{H_2})$ plot, Model A is confirmed.

Henry's Constant

In the kinetic models we need the concentrations in slurry phase, but what can be calculated first from the experimental data are usually the partial pressures in the product. The relation between the concentration and the partial

pressure of a specific species is given by the Henry's law:

$$P_i = H_i C_i \quad (10)$$

Where H_i is the Henry's constant for species i . Nettelhoff et al (1985) discussed the Henry's constant for Fischer-Tropsch in the slurry phase, and gave the expression of it in the form

$$H_i = a_i \exp\left(\frac{d_i}{T}\right) \quad (11)$$

Where the parameters a 's and d 's are given for H_2 , CO, CO_2 and H_2O .

Calculation of the Partial Pressures

Huff and Satterfield (1984b) showed the method of calculating the partial pressure by product mean value of m and n and conversions. The equations to be used are:

$$P_{H_2} = \frac{P[F - (m+n)z + y]}{F + 1 + (1-m-n)z} \quad (12)$$

$$P_{CO} = \frac{P(1-nz-y)}{F + 1 + (1-m-n)z} \quad (13)$$

$$P_{CO_2} = \frac{Py}{F+1+(1-m-n)z} \quad (14)$$

$$P_{H_2O} = \frac{P(zn-y)}{F+1+(1-m-n)z} \quad (15)$$

Where z and y can be calculated by the relations

$$z = \frac{(1+F)X_{CO-N_2}}{2n+m} \quad (16)$$

$$y = X_{CO} - zn \quad (17)$$

Where P = Total pressure

F = inlet H_2/CO ratio, mole/mole;

Note now z and y are based on per mole of CO entering the reactor.

Summary of Procedure of Kinetic Model Selection

(a) Conduct experiments by using the same catalyst and at the same temperature, but varying the feed rate and/or H_2/CO inlet ratio, to get a series of data points;

(b) From the analysis of hydrocarbon products find the mean carbon number, n , the H/C ratio and thus m . A mass weighted average value can be taken of the various product streams (Ledakowicz et al, 1985);

(c) Find z and y and then the partial pressures using Equations (12) through (17);

(d) Calculate the concentrations by Henry's law, Equation (10);

(e) Test the validity of a specific model by plotting the data of concentrations in proper coordinates. If valid, get the rate parameters b 's.

Effect of Temperature

So far the effect of temperature has not been discussed except for that on the Henry's constant. The temperature effect on the rate parameters b 's in the kinetic models are usually expressed by the Arrhenius equation,

$$b_i = A_i \exp\left(-\frac{E_i}{T}\right) \quad (18)$$

Therefore by conducting experiments at several temperature levels and repeating the calculation procedure outlined above, we can get the variation of b 's with temperature and find the frequency factor A 's and the activation energy E 's in Equation (18). By now, a complete kinetic model is established.

CSTR MODEL

All of the kinetic models discussed above can be written in a common form:

$$-r_{CO_2} = kC_{CO_2} \quad (19)$$

See earlier equations 8
Also more complicated
cases. See next page

where k can be called reaction rate parameter. Unlike the rate constant in the first order expressions, k is a parameter which varies according to different kinetic models. Table 1 gives the proper expression of k for each kinetic model mentioned above.

Table 1. Rate Parameter k for Different Kinetic Models

Model	1st order	CO, only	H ₂ O only	CO, plus H ₂ O
k	b_1	$\frac{b_1}{1+b_1 \frac{C_{CO}}{C_{CO}}}$	$\frac{b_1}{1+b_1 \frac{C_{H_2O}}{C_{CO}}}$	$\frac{b_1}{1+b_1 \frac{C_{CO}}{C_{CO}} + b_2 \frac{C_{H_2O}}{C_{CO}}}$

Using the rate parameter thus defined, a model correlating the conversions with the system parameters and operation conditions for CSTR reactor can be developed. The principal assumptions for the model is that the mass transfer is infinitely fast. That is, no limitation due to mass transfer is assumed. As a rule of thumb, this is satisfied when the stirrer speed is larger than 700 rpm (Ledakowicz et al, 1984).

Note the reaction rate $-r_{CO}$ is based on per unit mass of catalyst, therefore

e.g. get an instantaneous conversion $\times \frac{\text{mole}}{\text{s} \cdot \text{g catalyst}}$

$$\text{rate } r_{CO} = \frac{1}{m_{cat}} \frac{dN_{CO}}{dt} \quad \text{or} \quad -r_{CO} m_{cat} = -\frac{dN_{CO}}{dt} \quad (20)$$

where m_{cat} = mass of catalyst, g

N_{CO}^0 = molar flow rate of syn-gas at inlet, mole/s.

Using Equation (19) we have

$$kC_{H_2}m_{cat} = X_{CO-H_2}N_{CO-H_2}^0 \quad (21)$$

By Henry's law

$H = \text{Henry's Constant}$

$$C_{H_2} = \frac{P_{H_2}}{H_{H_2}} = P \frac{w_{H_2}}{H_{H_2}} \quad (22)$$

where w_{H_2} is the molar fraction of H_2 at the outlet. Material balance of H_2 gives:

$$w_{H_2}^2 N^2 = w_{H_2}^0 N_{CO-H_2}^0 (1 - X_{H_2}) \quad (23)$$

Lewis thinks this term cancels out or you are relating mole fraction @ outlet to mole fraction at inlet and conversion. So mole fraction at outlet not used $\therefore$ not needed $\therefore$ don't need conc'n

where $N = PQ'/RT$, the molar flow rate of gas phase at the outlet, mol/s, with Q' gas phase being the volumetric flow rate at the outlet, m³/s. Using the relations

$$Q' = Q_{CO-H_2}^0 (1 + \alpha X_{CO-H_2}) \quad (24)$$

and

$$w_{H_2}^0 = F / (1 + F)$$

where α is the contraction factor, and F is the H_2/CO inlet ratio, mole/mole, we get from Equations (22) and (23),

$$C_{H_2} = \frac{RTN_{CO-H_2}^0}{Q_{CO-H_2}^0 H_{H_2}} \left(\frac{1 - X_{H_2}}{1 + \alpha X_{CO-H_2}} \right) \left(\frac{F}{1 + F} \right) \quad (25)$$

Substituting Equation (25) in Equation (21) gives

$$\frac{k m_{cat} RT}{H_{H_2} Q_{CO-H_2}^0} = \frac{X_{CO-H_2} (1 + \alpha X_{CO-H_2})}{1 - X_{H_2}} \left(1 + \frac{1}{F}\right) \quad (26)$$

Define the Damkohler number

$$Da = \frac{k m_{cat} RT}{H_{H_2} Q_{CO-H_2}^0} \quad (27)$$

and

$$\alpha = \alpha \frac{F(1+U)}{U(1+F)} \quad (28)$$

where U is the H_2/CO usage ratio. Also notice the relation between the conversions:

$$X_{CO-H_2} = \frac{F(1+U)}{U(1+F)} X_{H_2} \quad (29)$$

We finally get the desired model for CSTR reactors:

$$\frac{(1 + 1/U) X_{H_2} (1 + \alpha X_{H_2})}{1 - X_{H_2}} = Da \quad (30)$$

No mass transfer limitations

Lewis plotted this equation which is linear only when first order.

Used data set from Run 43

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Calculation of the Rate Constant.

(1)

Henry's Constant: (Nemethy et al., 1985)

For H_2 ,

$$H_{H_2} = 6.952 \cdot e^{555.1/T} \left(\frac{\text{MPa} \cdot \text{dm}^3}{\text{mol}} \right)$$

where T is in K

$$T = 256^\circ\text{C} = 538.15\text{ K}$$

$$H_{H_2} = 19.508 \left(\frac{\text{MPa} \cdot \text{dm}^3}{\text{mol}} \right)$$

Const.

From the plot. Let $f(x_{H_2}) = Y$ dimensionless

$$\frac{1}{Q_i} = X \left(\frac{\text{hr} \cdot \text{gFe}}{\text{nl}} \right)$$

$$Y = \text{Const.} \cdot X$$

Take two points: $(X, Y) = (0.833, 1.55), (0.2, 0.4)$

$$\text{Const.} = \frac{\Delta Y}{\Delta X} = \frac{1.55 - 0.4}{0.833 - 0.2} = 1.817$$

$$\text{Const.} = 1.817 \left(\frac{\text{nl}}{\text{hr} \cdot \text{gFe}} \right)$$

(2)

- Note the volume used is "nl" — liter at normal condition.
It needs to be converted to the volume at Rx condition:

	P	T
(a) Normal Cond.	1 atm. = 14.696 psia	20°C = 293.15 K
(b) Rx. Cond.	290 psig = 304.696 psia	265°C = 538.15 K

By $PV = nRT$

$$\frac{P_a V_a}{P_b V_b} = \frac{T_a}{T_b}$$

$$\therefore V_b = \frac{P_a}{P_b} \frac{T_b}{T_a} V_a$$

$$= \frac{14.696}{304.696} \frac{538.15}{293.15} V_a = 0.0285 V_a$$

$$\therefore \text{Const.} = 1.817 \times 0.0285 \left(\frac{\text{hr}}{\text{g Fe}} \right)$$

$$\boxed{\text{Const.} = 0.161 \left(\frac{\text{hr}}{\text{g Fe}} \right)}$$

• Rate Constant k

$$f(x_{H_2}) = \text{Const.} \cdot \left(\frac{1}{Q} \right)$$

$$\text{Const.} = \frac{k RT}{H_{H_2} (1 + \frac{1}{Q})}$$

$$\therefore k = \text{Const.} \cdot \frac{H_{H_2} (1 + \frac{1}{Q})}{RT}$$

$$U = 0.578 \quad R = 8.314 \left(\frac{J}{\text{mol} \cdot K} \right)$$

$$k = 0.161 \left(\frac{L}{\text{hr} \cdot \text{gFe}} \right) \times \frac{19.508 \left(\frac{\text{MPa} \cdot \text{dm}^3}{\text{mol}} \right) (1 + \frac{1}{0.578})}{8.314 \left(\frac{J}{\text{mol} \cdot K} \right) \cdot 538.15(K)}$$

$$= 1.916 \times 10^{-3} \left(\frac{L \cdot \text{MPa} \cdot \text{dm}^3}{\text{hr} \cdot \text{gFe} \cdot J} \right)$$

$$\text{Note: } \text{MPa} \cdot \text{dm}^3 = 10^6 \frac{N}{\text{m}^2} \cdot 10^{-3} \cdot \text{m}^3 \\ = 10^3 \text{ Nm} = 10^3 J$$

$$\therefore k = 1.916 \times 10^{-3} \frac{10^3 J \cdot L}{\text{hr} \cdot \text{gFe} \cdot J} = 1.916 \frac{L}{\text{hr} \cdot \text{gFe}}$$

$$\text{or } k = 0.532 \left(\frac{\text{cm}^3}{\text{s} \cdot \text{gFe}} \right)$$

Comparison with Data in Literature

If ignore the effect of CO_2 , the data by Ledakowicz et al.

(1985) gives:

T (K)	(°C)
493	220
513	240
523	250
533	260

UOP data:

538	265
-----	-----

$$k \left(\frac{\text{cm}^3}{\text{s.g cat.}} \right)$$

0.161
0.828
0.836
0.965

1.3% K. in Cat.

$$0.532$$

$$\left(\frac{\text{cm}^3}{\text{s.g Fe}} \right)$$

do not change
our method of
calc.

Not correct
just compare
our Ledakowicz
experiment with
his

CSTR MODEL: PLANT 700B TESTS

f(H₂ Conv.) vs. Residence Time

265 C, Alpha=-0.5

Final Form
1/6/52

Final Form

$f(x_{n+1})$

Final Form
(1/6/52)

Final Form

1.	0.054	12.51	76.0	5.415	0.5	1.756
2.	0.263	11.62	73.0	4.265	0.9	1.111
3.	0.110	8.77	61.0	2.878	1.20	0.333
4.	1.000	2.00	31.0	2.000	2.00	0.5
5.	1.200	2.70	32.0	1.197	2.80	0.333
6.	1.275	3.62	32.0	1.000	2.90	0.345
7.	0.550	2.92	32.0	1.000	2.60	0.333

70	5.876	1.2	0.333
75	9.86	1.2	0.333
80	2.81	2.4	0.333
85	1.56	3.8	0.333
90	1.01	5.2	0.333
95	0.93	6.7	0.333

About a single test or a few tests at similar conditions:

(A) Rate Constant

If we assume:

- 1st order reaction (w.r.t. H_2)
- Conversions $\rightarrow 0$ as feed rate $\rightarrow \infty$

Then: a single test can be used in conjunction with the CSTR model to find the rate constant:

$$f(x_{H_2}) = \frac{k R T}{H_{H_2} Q_0}$$

② Activation Energy:

Rate constant is usually expressed as a function of T :

$$k = a e^{-\frac{b}{RT}}$$

where b is called activation energy.

Then CSTR Model gives

$$f(X_{H_2}) = \frac{a e^{-\frac{b}{RT}} \cdot RT}{a \cdot e^{-\frac{b}{T}} \cdot \dot{Q}^0} = (\bar{A} e^{-\frac{\bar{B}}{T}}) \frac{T}{\dot{Q}^0}$$

$$\ln[f(X_{H_2}) \dot{Q}^0] = \ln \bar{A} + \ln T - \frac{\bar{B}}{T}$$

At least, two tests are needed at two different T 's to get the two unknowns $\bar{A}$ & $\bar{B}$.

From ① & ②:

To find	Minimum # of Tests:
k	1.
Activation Energy	2 at different T 's

2/20/92

Estimation of C_{CO_2}/C_{CO}

Plant 700B Run 43

S_{CO_2} CO_2 selectivity

X_{CO} CO conversion

In this Run 43. $S_{CO_2} \approx 0.95$ (± 0.025)

$$X_{CO} = 0.2 \sim 0.85$$

$\therefore$ In the out flow. (product)

$$\frac{y_{CO_2}}{y_{CO}} = \frac{X_{CO} \cdot S_{CO_2}}{1 - X_{CO}} = \frac{0.09 \sim 0.38}{0.15 \sim 0.8} = 0.11 \sim 2.53$$

Henry's Constant

By Nettelhoff et al (1985).

$$H_{e,i} = \frac{P_i}{C_i}$$

Partial pressure
little same as
molar fraction

we are pushing
less CO_2 than they are
ad less CO_2 might near
less CO_2 interface
why we get it.
line 129

2/25/72 - (2)

For CO. $H_{CO} = 9.152 e^{248/T} \left(\frac{\text{MPa} \cdot \text{l}}{\text{mol}} \right)$

In our case $T = 265^\circ\text{C} = 538 \text{ K}$

$H_{CO} = 9.152 e^{248/538} = 14.51 \left(\frac{\text{MPa} \cdot \text{l}}{\text{mol}} \right)$

For CO₂. $H_{CO_2} = 22.64 e^{-\frac{6247}{T}} \left(\frac{\text{MPa} \cdot \text{l}}{\text{mol}} \right)$

In our case $H_{CO_2} = 22.64 e^{-\frac{6247}{538}} = 7.72 \left(\frac{\text{MPa} \cdot \text{l}}{\text{mol}} \right)$

$$\frac{C_{CO_2}}{C_{CO}} = \frac{P_{CO_2}/H_{CO_2}}{P_{CO}/H_{CO}} = \frac{P_{CO_2}}{P_{CO}} \frac{H_{CO}}{H_{CO_2}} = \frac{y_{CO_2}}{y_{CO}} \frac{H_{CO}}{H_{CO_2}}$$

$\therefore \frac{C_{CO_2}}{C_{CO}} = (0.11 \sim 2.53) \frac{14.51}{7.72} = 0.21 \sim 4.76$

Ledakowicz et al's case.

$T = 260^\circ\text{C}$

$\frac{y_{CO_2}}{y_{CO}} = 0.78 \sim 4.21$ (from Table I)

$\frac{C_{CO_2}}{C_{CO}} = 1.5 \sim 8.6$ (from Fig. 8)

$\therefore \text{Then } \frac{H_{CO}}{H_{CO_2}} = \frac{C_{CO_2}/C_{CO}}{y_{CO_2}/y_{CO}} = \frac{1.5 \sim 8.6}{0.78 \sim 4.21} = 1.9$

very close to the values used in our case

2/25/92 — (3)

Rate constant from Ledakowicz et al.

$$-r_{\text{CO}+\text{H}_2} = k \cdot \frac{C_{\text{H}_2}}{1 + 0.115 \frac{C_{\text{CO}_2}}{C_{\text{CO}}}}$$

Compared with 1st order case

$$-r_{\text{CO}+\text{H}_2} = b_1 C_{\text{H}_2}$$

We can define an "equivalent rate constant" k_{eq}

$$k_{\text{eq}} \equiv \frac{k}{1 + 0.115 \frac{C_{\text{CO}_2}}{C_{\text{CO}}}}$$

They gave:

$$k_{\text{eq}} = \frac{1.8 \times 10^{11} e^{-\frac{12967}{T}}}{1 + 0.115 \frac{C_{\text{CO}_2}}{C_{\text{CO}}}}$$

In our case, $T = 538 \text{ K}$. $\frac{C_{\text{CO}_2}}{C_{\text{CO}}} = 0.21 \sim 4.76$ then

this gives:

$$k_{\text{eq}} = 0.87 \sim 1.32$$

ours: $k_1 = 0.532$

F-T CSTR MODEL TEST

f(H₂ Conv.) vs. Residence Time

Reference data taken from Ledakowicz
et al. (1985)

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ATTACHMENT

**AUTOCLAVE TESTING OF UCI CATALYSTS
IN SUPPORT OF THE
F-T TRIAL RUN IN A SBCR**

R. R. Frame and H. B. Gala

**UOP
DES PLAINES, ILLINOIS**

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The objective of this work was to provide support for the trial Fischer-Tropsch (F-T) run that was carried out in the slurry bubble-column reactor (SBCR) at the LaPorte Alternative Fuels Development Unit. UOP support consisted of: autoclave (continuous stirred-tank reactor) testing for catalyst evaluation and correlation of autoclave data with SBCR data. A total of seven different runs with six different catalysts were carried out. Information collected during this support activity is discussed in two parts in this report. Part I of this report describes the seven runs carried out and Part II compares the performance of the catalyst in autoclave with that observed in the SBCR.

PART I.

SUMMARY OF AUTOCLAVE RUNS

Five catalysts prepared by United Catalysts Inc. (UCI) were evaluated in a slurry autoclave plant at UOP. These catalysts were prepared as potential catalysts for use in the SBCR demonstration run at LaPorte, Texas. The initial catalyst (UCI "O") was prepared to have the same composition as a commercially available Ruhrchemie catalyst which was also evaluated as part of this work. The fifth catalyst ("Composite" catalyst) was the one actually used in the LaPorte run.

The UCI "O" catalyst composition and performance differed from the Ruhrchemie catalyst necessitating preparation of additional catalysts. Specifically, the UCI "O" catalyst was less selective for light ends than the Ruhrchemie catalyst. The objective in preparing the subsequent catalysts was low wax production (high light ends production). The reason was that catalyst/wax separation was expected to be a key problem in SBCR operation. It was presumed that low wax-producing catalysts will not put as much stress on the separation process (filtration).

All catalysts evaluated were four component catalysts, that is they all contained iron, copper, silicon and potassium in their oxide form. Catalyst compositions are summarized in Table 1.

For the tests carried out with the Ruhrchemie (Run 31), UCI "O" (Runs 44 and 48), UCI "A" (Run 50), UCI "B" (Run 51), and UCI "Start-up" (Run 53) catalysts, UOP's standard procedure for activation and testing was used. The slurry autoclave reactor used for these runs is operated in a hot box which is maintained at 130°C. A schematic of the plant as it was operated in Runs 31 and 44 is shown in Figure 1. For Run 48 and onwards a second trap was added to the hot box so that overhead condensate from the product gas and wax from the periodic wax withdrawals could be trapped separately. A schematic of this modified configuration is shown in Figure 2. The hot box traps are maintained at a pressure 5 psi less than the autoclave. Feed is added continuously below the level of liquid in the reactor. Overhead gas is removed continuously from the reactor, the part of it that does not condense in the hot box trap is taken first into a trap which is maintained at 0°C and 50 psig followed by a -78°C trap (atmospheric pressure). Slip streams of the gas leaving the 130°C hot box and the 0°C trap are analyzed with on-line GC analyzers by, respectively, boiling point and gas type analyses.

The liquid level in the autoclave is maintained at a constant level by periodic withdrawals of wax. This wax is taken into the train of traps described above.

The autoclave was loaded with 72.7 g of the as received catalyst and 290 g of Ethylflo™ 164 (a C₃₀ oil obtained from the Ethyl Corporation). The catalyst was activated by heating it to 280°C under a nitrogen atmosphere. After pressure testing the plant, the feed syngas blend which is made up of hydrogen, carbon monoxide and argon in the molar ratio 0.7:1.0:0.1 is introduced. Argon is used as an internal standard. The catalyst is then reduced for a period of 12 hr. The syngas feed rate, and reactor temperature and pressure were maintained at 2 NI/hr/gFe, 280°C and 153 psig, respectively during this 12-hr period. During the remainder of the run the feed rate, temperature, and pressure were controlled at 2.4 NI/hr/gFe, 265°C and

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290 psig, respectively. In Run 53, as will be discussed below, condition changes were made during the run. These conditions are noted at the top of the figures which summarize the performance of each individual catalyst (See Appendix A).

Run 31

This run was performed with a commercially available Ruhrchemie catalyst. The performance of this catalyst at line-out conditions (time-on-stream: 240 hr) is summarized in the material balance data presented in Table 2. Detailed run summary data are illustrated in Appendix A, Figures A-1 through A-7. These run summary plots show that after pretreatment this catalyst still required 200 hours to reach a stabilized conversion. During this 200 hours the conversion gradually increased. UOP catalysts tested previously under DOE contracts have reached a stable conversion quicker than the Ruhrchemie catalyst and during the time before line out have lost, not gained, activity. However, the UOP catalysts have a different composition than the Ruhrchemie catalyst. It is possible that the pretreatment conditions used were not adequate to fully activate (reduce) the Ruhrchemie catalyst.

In Run 31, the methane and ethane selectivities (Figures A-4 and A-5) increased throughout the 200 hr line-out period. The sum of the methane and ethane selectivities at line-out was 7.6 mole %. This is a fairly high number compared to the UCI catalysts discussed below. However, it is not extraordinary compared to historic Fischer-Tropsch catalysts.

The $H_2:CO$ usage ratio decreased from 0.73 to 0.68 during the 200 hour line-out period. Plots of $H_2:CO$ usage ratio versus $CO + H_2$ conversion are available. For instance, the curve in Figure 3 resulted from Run 43; a run performed as part of UOP's DOE contract but with a UOP-prepared catalyst. During this run, after line out was achieved, feed rate changes were made to vary the conversion. The small change in the usage ratio in Run 31 resulted not after but during the line-out period. The $CO + H_2$ conversion changed from 67% to 70%. The change in usage ratio might not be solely due to the different conversions during line-out period and it is possible that the change in product composition during this period is also contributing to the observed change in the usage ratio. A lower usage ratio will result if the olefinicity of the products is increasing or if the slope of the Schulz-Flory plots for the heavier products is flattening out. Data for Run 31 show that during the line-out period, methane selectivity is increasing and the olefin to paraffin ratio for C_2 to C_4 (Figures A-5 to A-7) is decreasing. This is indicative of a higher, not lower, $H_2:CO$ usage ratio. So the observed decrease in lower $H_2:CO$ usage ratio may be due to the change in the selectivity of the heavier products.

Run 44

This run used a catalyst prepared by UCI (catalyst "O") which was targeted to have the same composition as that of the Ruhrchemie catalyst. The compositions of the two catalysts were

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similar but not the same; the UCI "O" catalyst had more potassium (4.1 versus 1.4 wt%, Table 1) than the Ruhrchemie catalyst.

The Ruhrchemie and UCI "O" catalysts were evaluated under identical conditions. The performance of the UCI "O" catalyst is summarized in Figures A-8 to A-14 and a summary material balance for line-out conditions at 475 hrs-on-stream (HOS) is presented in Table 3. There were performance differences between these two catalysts tested in Run 31 and Run 44. The UCI "O" catalyst began at a very high conversion (80% CO conversion, Figure A-8) but lost activity as the run progressed, whereas the Ruhrchemie catalyst started at a lower conversion and gained activity. Run 31 was shorter than Run 44 but in both runs the catalysts' activities appeared to be lining out at run's end. The activities of these two catalysts were similar at line-out with the Ruhrchemie catalyst perhaps being slightly more active.

Part way through Run 44 a new lot of feed (Feed B) was received. When it was introduced at 225 HOS there appeared to be a step loss in activity. A small amount of the original feed (Feed A) was left and when it was re-introduced there appeared to be an increase in activity. Although it would appear that there was something in the feed which caused a reversible deactivation, attempts to determine what it was through feed analysis were unsuccessful (Table 4).

Both the Ruhrchemie and UCI "O" catalyst became increasingly selective for methane (Figure A-4 and A-11) as the runs progressed. The UCI "O" catalyst was about 1% less selective for methane than the Ruhrchemie catalyst at any time on stream. The ethane selectivities for Runs 31 and 44 had not lined-out by runs' end. Again, the UCI "O" catalyst was less selective to ethane. The sum of the methane and ethane selectivity was 5.2% at the end of Run 44.

The $H_2:CO$ usage ratio was 0.58 for the majority of the run whereas for Run 31 it decreased from 0.73 to 0.68 as the run progressed. Although less light weight material (for instance, methane) was produced in Run 44 than in Run 31, this was compensated for by the higher olefinicity (higher olefin:paraffin ratio) of the light products formed during Run 44. The UCI catalyst was likely less able to hydrogenate olefins than the Ruhr catalyst.

Run 48

This run used a fresh sample of the UCI "O" catalyst that was also used in Run 44. The performance of the catalyst during this run is summarized in Figures A-15 to A-22 and material balance data for the two different periods are shown in Tables 5 and 6. The conditions at the outset were the same as Run 44, however, the initial conversions were different for reasons which are not yet clear. It is possible that this was caused by slight, undetectable, differences in the activation procedure during the two runs. However, the conversions were about the same by 75 HOS, since during Run 44 there was a continual loss in activity, whereas, during Run 48 the conversion was relatively constant. There was a temperature spike at 75 hours, although it

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registers at 317°C (Figure A-16), it is possible that even higher temperatures were attained before the operator recorded this high temperature. It appears that the temperature spike was sufficiently high to cause some irreversible loss of activity. The CO conversion was 70% before the spike and 60% after.

The effect of an increase in temperature on catalyst performance was determined near the end of the run. Clearly a conversion increase can be obtained through temperature increase. Furthermore, the catalyst ran stable at this higher temperature, perhaps because the increase in temperature was not as great as the earlier temperature spike which might have taken the edge off the catalyst.

The conversions/selectivities for Runs 44 and 48 are compared in Table 7. The reproducibility was not as good as expected based on previous work with UOP catalysts in the slurry autoclave. The CO conversion at 70 hours, which was just before the temperature spike, was 70%, at this time the run 44 CO conversion was 78%. There were also differences in the selectivities, for instance the methane selectivity for Run 44 was 3.6% versus 5.4% for Run 48. The reasons for these differences are not known. Earlier studies of plant reproducibility indicated better reproducibility than this. It is unfortunate that the temperature spike occurred, because it appeared that the Run 48 CO conversion was holding at 70% whereas the Run 44 CO conversion dropped from a high initial conversion of 80% to a lined out CO conversion of 60% at 500 hours. Perhaps the differences between the two runs would not have been as great if it was possible to compare them when they were lined out.

Table 7 also shows a slight difference between the $H_2:CO$ ratios for the two runs, this usage ratio was 0.62 for Run 48 versus 0.58 for Run 44. This difference is slight and assigning an explanation to it might be tenuous.

A Schulz-Flory plot is attached as Figure 4. Figure 5 is a plot of the Schulz-Flory data up to carbon number 16 and a curve fitted to the data using a non-linear regression model. The calculated α_1 and α_2 were, respectively 0.52 and 0.92. Figure 6 illustrates product distribution obtained during 144 to 163 HOS in Run 48.

The $H_2:CO$ usage ratio was 0.62 before the temperature spike and 0.63 after it. The usage ratio dropped back to 0.62 after the temperature increase from 265°C to 285°C. These usage numbers were close to those observed for Run 44. The small differences in the case of these two runs could have been due to the slightly different conversions.

Run 50

This run used the UCI "A" catalyst (Table 1). Summary material balance data at the end of the run are shown in Table 8 and the conversion and selectivity data are shown in Figures A-23 to A-29. There was a continuous loss in activity over the 280 hour run. The final CO conversion

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was 47%. The methane selectivity was low throughout the run and did not vary much as the run progressed (Figure A-26), this selectivity was about 2.8%. The ethane selectivity was also low and did not vary much as the run progressed (Figure A-27), this selectivity was 0.7%. The sum of the methane and ethane selectivities was 3.5% which is very low.

The $H_2:CO$ usage ratio varied from 0.57 to 0.60 from the beginning to the end of the run (Figure A-24). This usage ratio is closer to that observed in Runs 44 and 48 than in Run 31. Although of different composition catalysts UCI "O" and UCI "A" were less prone to hydrogenate olefins than the Ruhrchemie catalyst, thus the lower $H_2:CO$ usage ratio and the higher olefin to paraffin ratios with the UCI catalysts. Also both UCI catalysts produced less methane which is hydrogen rich compared to all other products.

The UCI "A" catalyst did not have the hoped for properties, namely high selectivity for gaseous products. In fact, this catalyst was among the lowest yet tested at UOP for light gas production. That coupled with the apparent instability of this catalyst forced the preparation of additional catalysts by UCI.

Run 51

This run used UCI "B" catalyst, its performance is outlined in Figures A-30 to A-35 and material balance at line-out conditions is summarized in Table 9. Unlike catalyst UCI "A", this catalyst was quite stable. The CO conversion was 60% which is the same as the line-out conversion for UCI "A" catalyst in Run 50. The ultimate selectivities for light products were high, characteristic of a low wax-producing catalyst; however, it took ten days to achieve high light end selectivity.

The $H_2:CO$ usage ratio was about 0.65, which is the highest of the three UCI catalysts. This catalyst produced a higher level of) than the previous two and also had a lower olefin to paraffin ratio for the C_2 to C_4 olefins (Figures A-33 to A-35).

Even though the selectivities to light products increased markedly during this run (5.9% methane conversion at line-out, Figure A-33), the $H_2:CO$ usage ratio was consistently at 0.61 to 0.62. Although the catalyst selectivity performance was obviously changing during this period the $CO + H_2$ conversion was nearly constant. The effects of the selectivity changes (more methane, more olefins) may have counterbalanced resulting in a stable usage ratio.

After comparing the first three UCI catalysts ("O", "A", and "B") it was decided that the commercial-scale preparation for the LaPorte SBCR test should follow the recipe of the first catalyst (UCI "O" tested in Runs 44 and 48). UCI "A" catalyst (Run 50) produced more wax (less methane) than UCI "O" (Run 44 and 48). Although the ultimate performance of UCI "B"

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catalyst (Run 51) was superior to UCI "O" and "A" (for the objectives of the run of testing a low wax-producing catalyst), it took ten days in Run 51 to achieve this performance. Since the LaPorte test was going to last about twenty days, a ten day line-out period was considered too long.

Run 53

This run used UCI "Start-up" catalyst. It is a sample from an aliquot that UCI withdrew from the initial several hundred pound portion of their commercial-scale production run of catalyst for the August, 1992 slurry bubble-column reactor run at LaPorte, Texas. The composition of this catalyst was not the same as the catalyst from the main part of the run, UCI "Composite" catalyst. The "Composite" catalyst was loaded into the SBCR at LaPorte and was tested at UOP in Run 54.

The performance of the "Start-up" catalyst is summarized in Figures A-36 to A-41 and material balance for three different conditions is summarized in Tables 10 to 12. Run 53 started at the conditions (265°C, 290 psig, and 2.4 NI/hr/gFe) which had been used for the runs with the Ruhrchemie and UCI "O", "A", and "B" catalysts. However, after the plant had been on stream for 120 hours a series of condition changes were made to determine catalyst performance under conditions that were planned to be used at LaPorte. During the final part of the run the plant was returned to the initial conditions to find out if the performance had degraded during the run.

At the time of the first condition change at 120 hours the catalyst appeared to have reached line out at 63% CO conversion and 3.3 mole % methane selectivity. Decreasing the pressure from 290 to 200 psig resulted in a decrease in conversion to 50% and about a 0.5% increase in the methane selectivity (Table 10). Increasing the feed rate from 2.4 to 5.0 NI/hr/gFe caused 50% loss in conversion and an increase in the methane selectivity of close to 1%. Next the plant pressure was increased to 400 psig at the same high feed rate. This resulted in an increase in CO conversion to 48%, but little change in the methane selectivity (Table 11). Finally, the plant was brought back to the initial conditions in two steps, first a decrease in the feed rate from 5 to 2.4 NI/hr/gFe and then a decrease in plant pressure (from 400 to 200 psig), the combined effect of which was an increase in conversion to 55% and a decrease in methane selectivity to 2.1%. The final step was an increase in plant pressure to 290 psig which brought the conversion back to where it was at 120 hours, however, the methane selectivity was 3.0% versus the earlier 3.5% (Table 12). The selectivity to the other light hydrocarbons (C₂ to C₄) also decreased between 120 hours and the end of the run. Apparently the aging process did not change the conversion but did shift the selectivity toward heavier products.

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Run 54

This run used the UCI "Composite" catalyst which is an aliquot of the 800 lb batch of catalyst that was loaded in the LaPorte SBCR. This catalyst was of finer mesh size than other catalysts used in this study. The "Composite" catalyst is believed to have at least some particles <10 microns.

The activation procedure used for Run 54 was similar to that used for the LaPorte SBCR run; however, it was different from that used in Runs 31, 44, 48, 50, 51, and 53. Initially the catalyst was heated in nitrogen to 200°C and then a gas mixture containing 25% nitrogen and 75% syngas was used to raise the reactor temperature to 280°C. The reactor pressure was maintained at 150 psig. After 12 hours at 280°C, the pressure, temperature, gas composition, and gas flow rate were changed to bring the reactor to the baseline operating conditions. UOP followed the run plan for the LaPorte run and tested the UCI "Composite" catalyst at four different conditions:

1. baseline (200 psig, 265°C temperature, gas flow rate of 2.5 nL/h/g-Fe),
2. high gas flow rate (200 psig, 265°C temperature, gas flow rate of 5.5 nL/h/g-Fe),
3. high pressure (400 psig, 265°C temperature, gas flow rate of 5.95 nL/h/g-Fe), and
4. baseline-revisited (200 psig, 265°C temperature, gas flow rate of 2.97 nL/h/g-Fe).

The feed to the autoclave reactor consists of 6 mole% argon as internal standard so the syngas flow is lower than the total gas flow rate. Also, as will be discussed below, during the run some catalyst was inadvertently lost, and as a result the space velocities are higher than intended.

There were operational problems during this run which were in part due to the small particle size of the catalyst. At approximately 180 HOS, the 0.5 micron filter on the gas outlet line plugged. At the same time the operators were experiencing difficulties with the thermocouple which is used to monitor the temperature change across the gas/liquid interface within the autoclave. Because of this the position of the liquid level was not known, and as a result the liquid level reached the top of the autoclave and might, in fact, have caused the plugging of the gas outlet filter. The normal way of opening a plug, namely back purging with feed failed. This necessitated bypassing the filter, i.e. removing whatever was present in the top of the autoclave without filtering. When the liquid level reached the top of the autoclave it began to exit through the unfiltered gas outlet line. This resulted in wax and catalyst entering the 130°C trap which normally only accumulates small amount of condensate (liquid) present in the product gas. Figure 7 contains a plot of the amount of material in this trap as a function of time. The overflow apparently began about 200 hrs when higher than expected weights were recovered from this trap. Confirming this was the observation that the trap material was not a liquid but a solid wax similar in texture to the wax in the other hot box trap which collects material from

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the periodic liquid (wax) withdrawals. The amount of catalyst lost from the reactor was determined by calcining the recovered wax. The catalyst weights so determined are also plotted in Figure 7. Of the original 72.7 grams of catalyst, 11.4 grams were lost during the time wax overflowed into the hot box trap. By 300 HOS the plant operators were once again able to determine the position of the wax and had re-established the target wax level.

The filters on the wax outlet line functioned during the entire run. This is not too surprising because there are two wax filter assemblies each with two filters, whereas there is only one gas filter assembly and it only has one filter (Figure 1). During the LaPorte run the wax outlet filters plugged during the first two hours of use and could not be reopened. However, the flux through the LaPorte wax outlet filters was higher than through the UOP slurry autoclave wax outlet filters.

During the time the plant overflowed condition changes were also being made. The timing of the condition changes and the conversions and product selectivities are in Figures A-42 to A-48. Material balance information for each condition change is also shown in Tables 13 to 16. A problem with the on-line gas analysis resulted in loss of about 225 hr of selectivity data. The initial conversions were high, as high as conversions with the best previous catalysts evaluated at UOP and also higher than resulted from any of the previous UCI or Ruhrchemie catalysts tested at UOP. The catalyst used in this run contained some very fine mesh catalyst (<10 microns). The UOP catalysts were always sieved before use (through 40, on 400 mesh) to give granular catalyst pieces of about 40 to 150 micron in size. It is possible that the very small particle sizes present in the UCI "Composite" catalyst caused high conversion.

The objective in making this UCI catalyst was to make a high- α catalyst, namely one which makes high levels of light products, including methane, and low levels of wax. The initial selectivities illustrate that just the opposite happened and the catalyst produced a very low level of methane. The methane selectivities during this run are compared to methane selectivities in some previous runs on this autoclave plant in Figure 8. The comparison catalysts were all prepared at UOP as part of the current contract as low methane-producing catalysts. It is obvious that the UCI catalyst compares favorably to these previous catalysts as a low methane-producing catalyst.

Because the operational problems came at 200 hours, comparisons between Runs 53 and 54 should be made at times before 200 hours. The final plan for the LaPorte run was to operate at 200 psig plant pressure, therefore, Run 54 began at this pressure rather than 290 psig. Thus to make a direct comparison between Runs 53 and 54 requires use of Run 53 data after the pressure was decreased to 200 psig at 130 hours. At this time during Run 53 the CO conversion was 53% and the methane selectivity was 4.0 mole %, compared to 80% CO conversion and probable about 3.2 mole % during Run 54. Because of the on-line analyzer problems 130 hour selectivity data for Run 54 must be obtained by extrapolating 100 hour selectivity data.

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The two samples of catalyst from the UCI production run differed both in elemental analysis and performance. The "Composite" sample was more active than the "Start-up" catalyst. The "Composite" also appeared to be the finest mesh of all the UCI catalysts; this might have contributed to its high activity. The fine size probably also contributed to the plugging of the gas filter.

Table 7 shows a comparison of the initial (70 HOS) conversions and selectivities obtained for all the catalysts tested at UOP in support of the LaPorte SBCR run. Among all the catalysts, the "Composite" catalyst had the highest conversion (at a lower pressure) and the second lowest $C_1 + C_2$ selectivity.

PART II

COMPARISON OF SLURRY AUTOCLAVE DATA WITH SLURRY BUBBLE COLUMN DATA

As discussed earlier, UOP slurry autoclave Run 54 was carried out with UCI "Composite" catalyst that was tested in the SBCR at LaPorte.

Calculations of Kinetic Parameters

With the assumptions that: (a) the reaction rate is first order with hydrogen concentration and (b) there is no mass transfer resistance in the slurry autoclave, the kinetic parameters were calculated from the data collected in the slurry autoclave pilot plant. Results of these calculations for the four operating conditions of Run 54 are shown in Tables 17 to 20. As discussed before, during Run 54 some catalyst was inadvertently lost. Corrections were made to account for the catalyst that was lost from the reactor but was recovered in the product.

Comparison with Slurry Bubble-Column Data

Two models were used to calculate the performance of the "Composite" catalyst in the LaPorte SBCR:

- a. Model 1 - both the gas and the liquid are assumed to be in plug flow, and
- b. Model 2 - the gas phase is assumed to be in plug flow and the liquid phase assumed to be perfectly mixed.

Bukur's correlation was used to calculate the gas hold-up and Akita-Yoshida correlations were used to calculate the mass transfer coefficients. The liquid phase mixing and volume contraction (α) factor was set at -0.5.

Kinetic information obtained from Run 54 for baseline conditions (Table 17) were used to predict the performance of LaPorte SBCR Run AF-R6.1-A to Run AF-R6.1-H. The solid concentration in the model calculations was adjusted to match the model column space velocity with the experimental value. A trial and error method was used to calculate hydrogen conversion in the reactor. Once the hydrogen conversion was set, other conversions and productivity numbers were calculated.

Similar procedure was followed to predict the LaPorte SBCR performance in Runs AF-R6.2, AF-R6.3, and AF-R6.4 from the data obtained in Run 54 for high gas flow rate (Table 18), high pressure (Table 19), and baseline-revisited (Table 20) conditions, respectively. A summary of calculations for each run conditions are shown in Tables 21 to 34. The results predicted by the models are compared with the observed SBCR performance in Figures 9 to 11.

AUTOCLAVE TESTING OF UCI CATALYSTS

UOP

Observations and Conclusions

1. In Run AF-R6.1, the loss in CO conversion (Figure 9) with increasing HOS (at the same inlet gas velocity) is due to the continuous loss of catalyst from the reactor.
2. When the gas velocity is doubled from 0.13 fps in Run AF-R6.1 to 0.27 fps in Run AF-R6.2, the conversion drops by almost one-half (Figures 9 and 10). The effect of doubling the reactor pressure from 200 to 400 psig in Run AF-R6.3 is not as pronounced because the conversion from Run AF-R6.2 to Run AF-R6.3 increases by only about 66%. Previous studies in Fischer-Tropsch synthesis have also made similar observation on the effect of pressure.
3. Run AF-R6.1 and AF-R6.4 are carried out under similar pressure, temperature, and gas velocity. However, significant quantities of the catalyst is lost during the run resulting in an increase in the space velocity. The observed performance of catalyst in Run AF-R6.1 and AF-R6.4 almost falls on a straight line which is consistent with the increase in the space velocity. Also, the CO conversion rate obtained at the end of Run AF-R6.1 and Run AF-R6.4 is same. These data would suggest that there was no catalyst deactivation in the SBCR; however, it is hard to say so conclusively. In the LaPorte SBCR, the catalyst was allowed to settle in the wax outside the reactor and then the concentrated catalyst/wax slurry was recirculated back to the reactor. This recirculation will bring "fresh" (less deactivated?) catalyst to the reactor and maintain (or increase) the activity of the catalyst in the reactor.
4. At lower space velocities (less than $4 \text{ Nm}^3/\text{hr}/\text{kg-Fe}$), Model 1 predicts higher conversions than Model 2. At higher space velocities, as might be expected, both models converge. Predicted conversions and CO conversion rates (Figures 9 to 11) are higher than that observed at LaPorte in Runs AF-R6.1 and AF-R6.2, and lower than that observed at LaPorte in Run AF-R6.4. For Run AF-R6.3, the predicted CO conversion rate is higher, while predicted conversions match with those observed.

FIGURE 1
SCHEMATIC DIAGRAM OF UOP SLURRY AUTOCLAVE PLANT

FIGURE 2
SCHEMATIC DIAGRAM OF UOP MODIFIED SLURRY AUTOCLAVE PLANT

FIGURE 3
EFFECT OF CO+H₂ CONVERSION ON H₂:CO USAGE RATIO

265 DEG C

□ RUN 43

FIGURE 4
SCHULZ-FLORY PRODUCT DISTRIBUTION FOR RUN 48 (144-163 HOS)

LIQS BY OFFLINE; GAS BY ONLINE ANALYSIS

FIGURE 5
NON-LINEAR REGRESSION OF S-F PRODUCT DISTRIBUTION
RUN 48 (144-163 HOS)

ALPHA 1=0.52; ALPHA 2=0.92; XI=6.2;
PHI=0.222

FIGURE 6
PRODUCT BREAK-DOWN FOR RUN 48 (144-163 HOS)

FIGURE 7
WEIGHT OF WAX AND CATALYST RECOVERED IN RUN 54

**CATALYST CALCINED DURING RECOVERY THERE-
 FORE WGT CAN BE COMPARED TO CAT LOADED
 WHICH WAS 72.7 G**

FIGURE 8
METHANE SELECTIVITY OF VARIOUS F-T IRON CATALYSTS

RUN 49 - OUR BEST

• RUN 43 + RUN 43 265 DEG C * RUN 37

□ RUN 54 (100 HRS) ◇ RUN 54 (500 HRS) x RUN 49

H₂:CO - 0.7. PRESSURE - 290 PSIG
TEMP - 265 DEG C UNLESS OTHERWISE NOTED

FIGURE 9
OBSERVED AND PREDICTED CO CONVERSION DATA

■ LaPorte Data *— Liq. PM

FIGURE 10
OBSERVED AND PREDICTED CO+H₂ CONVERSION DATA

FIGURE 11
OBSERVED AND PREDICTED CO CONVERSION RATE DATA

■ LaPorte Data —*— Liq. PM

TABLE 1
CATALYST CHARACTERISTICS

Catalyst	Ruh Chemie	UCI Catalysts				
		O	A	B	Start-up	Composite
UOP Run Number	31	44 & 48	50	51	53	54
Elemental Analyses (wt %)						
Fe						
Cu	43.8	46.0	60.4	58.9	53.6	54.9
K	2.2	2.3	0.8	0.8	4.0	4.0
Si	4.8	5.3	1.2	2.5	2.3	5.3
	1.4	4.1	0.7	0.8	1.4	3.7
Surface Area, m ² /g	313	232	167	169	136	95
Pore Volume, cc/g	0.53	0.50	0.18	0.20	0.30	0.28

TABLE 2
MATERIAL BALANCE FOR RUN 31 AT 240 HOS

Run No: 31		HOS: 240		Catalyst: RUHR CHEMIE	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole	
		Rx T, C	265		
Copper	5.07	K	538	Inlet, I	0.700
Potassium	3.08	Rx P, psig	290	Outlet, O	0.750
Silicon	10.96	kPa	2101	Usage, U	0.681
Wt of catalyst in Rx, g		72.70	Conversion and Selectivity		
Wt of Fe in Rx, g		41.20	CO Conversion		71.0
Wt % Fe in catalyst		56.66	H2 Conversion		69.1
Wt of start-up oil, g		290.00	H2+CO Conversion		70.2
Wt of Slurry, g		362.70	Selectivity to CO2		43.0
Vol. of Slurry, cm ^ 3		458.69	Selectivity to CH4		5.2
Wt % Solids in Rx		20.04	Selectivity to C2H6		2.5
Solids Conc., g/cm ^ 3		0.1584945			
Syngas Feed Rate,		Material Balances, mol/hr			
nL/h/gFe	2.256		In	Out	Converted
1E-5 mole/s/gFe	2.796	CO	2.439	0.707	1.732
mol/hr	4.146	H2	1.707	0.528	1.179
L/h/gFe	0.214	H2 + CO	4.146	1.236	2.911
Water-Gas Shift Equilibrium Calculations					
Equm. Cons. K = [CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]					
K = 65.141		H2O out =		0.009	mol/hr
mol/hr		Atomic Balance, mol/hr			
CO to CO2	0.745	C, in	2.439	H, in	3.415
CO to HC	0.987	Out	2.439	Out	3.415
CO to CH4	0.051	as CO2	0.745	as H2O	0.017
CO to C2H6	0.049	as HC	0.987	as HC	2.341
H2 to H2O	0.009	as CO	0.707	as H2	1.057
H2 to HC	1.171			as HCO	0.234
Mass Balance in g/hr			HCs Distribution, g/hr		
IN		OUT		Methane	
CO	68.320	CO	19.813	Ethane	0.742
H2	3.442	H2	1.065	Others	16.393
		CO2	32.772	Total	17.958
		H2O	0.154		
		HCs	17.958	Product H/C ratio	2.372
TOTAL IN	71.762	OUT	71.762	O/C ratio	0.237
HC Yield	HCs	C1+C2(p)	CO Conversion Rate, gmole/kg Fe/hr		
g/h/gFe	0.436	0.038	Syngas Converted, Nm ^ 3/hr/m ^ 3 Rx		42
g/nL syn	0.193	0.017	STY of C3+ in 24 hrs, kg/m ^ 3 Rx		142
					858

TABLE 3
MATERIAL BALANCE FOR RUN 44 AT 475 HOS

Run No:	44	HOS:	475	Catalyst:	UCI "O"
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole	
		Rx T, C	265		
Copper	4.32	K	538	Inlet, I	0.700
Potassium	8.63	Rx P, psig	290	Outlet, O	0.840
Silicon	7.92	kPa	2101	Usage, U	0.619
Wt of catalyst in Rx, g		72.70	Conversion and Selectivity		
Wt of Fe in Rx, g		41.37	CO Conversion		63.0
Wt % Fe in catalyst		56.91	H2 Conversion		55.7
Wt of start-up oil, g		290.00	H2+CO Conversion		60.0
Wt of Slurry, g		362.70	Selectivity to CO2		48.0
Vol. of Slurry, cm ^ 3		458.69	Selectivity to CH4		4.1
Wt % Solids in Rx		20.04	Selectivity to C2H6		1.0
Solids Conc., g/cm ^ 3		0.1584945			
Syngas Feed Rate,		Material Balances, mol/hr			
nL/h/gFe	2.256		In	Out	Converted
1E-5 mole/s/gFe	2.796	CO	2.450	0.906	1.543
mol/hr	4.164	H2	1.715	0.759	0.955
L/h/gFe	0.214	H2 + CO	4.164	1.666	2.499
Water-Gas Shift Equilibrium Calculations					
Equm. Cons. K = [CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]					
K =		65.141	H2O out =		0.010 mol/hr
mol/hr		Atomic Balance, mol/hr			
CO to CO2	0.741	C, in	2.450	H, in	3.429
CO to HC	0.802	Out	2.450	Out	3.429
CO to CH4	0.033	as CO2	0.741	as H2O	0.019
CO to C2H6	0.016	as HC	0.802	as HC	1.892
H2 to H2O	0.010	as CO	0.906	as H2	1.519
H2 to HC	0.946			as HCO	0.052
Mass Balance in g/hr			HCs Distribution, g/hr		
IN		OUT	Methane		0.528
CO	68.614	CO	25.387	Ethane	0.241
H2	3.457	H2	1.531	Others	11.611
		CO2	32.600	Total	12.381
		H2O	0.172		
		HCs	12.381	Product H/C ratio	2.357
TOTAL IN	72.071	OUT	72.071	O/C ratio	0.065
HC Yield	HCs	C1+C2(p	CO Conversion Rate, gmole/kg Fe/hr		37
g/h/gFe	0.299	0.019	Syngas Converted, Nm ^ 3/hr/m ^ 3 Rx		122
g/nL syn	0.133	0.008	STY of C3+ in 24 hrs, kg/m ^ 3 Rx		608

TABLE 4
ANALYSIS OF FEED FOR RUN 44

Component	Feed A	Feed B
CO, mole %	56	56
H ₂ , mole %	37	37
A, mole %	6	6
N ₂ , mole %	0.17	0.32
Total S, wppm	<1	<1

TABLE 5
MATERIAL BALANCE FOR RUN 48 AT 140 HOS

Run No: 48		HOS: 140		Catalyst:		UCI "O"	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole			
		Rx T, C	265	Inlet, I		0.700	
Copper	4.32	K	538	Outlet, O		0.890	
Potassium	8.63	Rx P, psig	290	Usage, U		0.590	
Silicon	7.92	kPa	2101				
Wt of catalyst in Rx, g		72.70		Conversion and Selectivity			
Wt of Fe in Rx, g		41.37		CO Conversion		62.0	
Wt % Fe in catalyst		56.91		H2 Conversion		52.3	
Wt of start-up oil, g		290.00		H2+CO Conversion		58.0	
Wt of Slurry, g		362.70		Selectivity to CO2		43.5	
Vol. of Slurry, cm ^ 3		458.69		Selectivity to CH4		6.5	
Wt % Solids in Rx		20.04		Selectivity to C2H6		2.8	
Solids Conc., g/cm ^ 3		0.1584945					
Syngas Feed Rate,		Material Balances, mol/hr					
nL/h/gFe	2.256			In	Out	Converted	
1E-5 mole/s/gFe	2.796	CO		2.450	0.931	1.519	
mol/hr	4.164	H2		1.715	0.818	0.897	
L/h/gFe	0.214	H2 + CO		4.164	1.749	2.415	
Water-Gas Shift Equilibrium Calculations							
Equm. Cons. K = [CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]							
K =		65.141		H2O out =		0.009 mol/hr	
mol/hr		Atomic Balance, mol/hr					
CO to CO2	0.661	C, in	2.450	H, in	3.429	O, in	2.450
CO to HC	0.858	Out	2.450	Out	3.429	Out	
CO to CH4	0.056	as CO2	0.661	as H2O	0.018	as H2O	0.009
CO to C2H6	0.048	as HC	0.858	as HC	1.775	as CO2	1.321
H2 to H2O	0.009	as CO	0.931	as H2	1.636	as CO	0.931
H2 to HC	0.888					as HCO	0.189
Mass Balance in g/hr				HCs Distribution, g/hr			
IN		OUT		Methane		0.895	
CO	68.614	CO	26.073	Ethane		0.722	
H2	3.457	H2	1.649	Others		13.495	
		CO2	29.075	Total		15.112	
		H2O	0.161				
		HCs	15.112	Product H/C ratio		2.069	
TOTAL IN	72.071	OUT	72.071	O/C ratio		0.220	
HC Yield	HCs	C1+C2(p	CO Conversion Rate, gmole/kg Fe/hr		37		
g/h/gFe	0.365	0.039	Syngas Converted, Nm ^ 3/hr/m ^ 3 Rx		118		
g/nL syn	0.162	0.017	STY of C3+ in 24 hrs, kg/m ^ 3 Rx		706		

TABLE 6
MATERIAL BALANCE FOR RUN 48 AT 180 HOS

Run No:	48	HOS:	180	Catalyst:	UCI "O"
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole	
Copper	4.32	Rx T, C	285	Inlet, I	0.700
Potassium	8.63	K	558	Outlet, O	1.100
Silicon	7.92	Rx P, psig	290	Usage, U	0.603
		kPa	2101		
Wt of catalyst in Rx, g			72.70	Conversion and Selectivity	
Wt of Fe in Rx, g			41.37	CO Conversion	80.6
Wt % Fe in catalyst			56.91	H2 Conversion	69.4
Wt of start-up oil, g			290.00	H2+CO Conversion	76.0
Wt of Slurry, g			362.70	Selectivity to CO2	45.0
Vol. of Slurry, cm ^3			458.69	Selectivity to CH4	7.7
Wt % Solids in Rx			20.04	Selectivity to C2H6	3.2
Solids Conc., g/cm ^3			0.1584945		
Syngas Feed Rate,		Material Balances, mol/hr			
nL/h/gFe	2.256		In	Out	Converted
1E-5 mole/s/gFe	2.796	CO	2.450	0.475	1.974
mol/hr	4.164	H2	1.715	0.524	1.190
L/h/gFe	0.222	H2 + CO	4.164	0.999	3.165
Water-Gas Shift Equilibrium Calculations					
Equm. Cons. K = [CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]					
K =		48.026	H2O out =		0.020 mol/hr
mol/hr		Atomic Balance, mol/hr			
CO to CO2	0.888	C, in	2.450	H, in	3.429
CO to HC	1.086	Out	2.450	Out	3.429
CO to CH4	0.084	as CO2	0.888	as H2O	0.041
CO to C2H6	0.069	as HC	1.086	as HC	2.340
H2 to H2O	0.020	as CO	0.475	as H2	1.048
H2 to HC	1.170			as HCO	0.177
Mass Balance in g/hr			HCs Distribution, g/hr		
	IN		OUT		
CO	68.614	CO	13.311	Methane	1.341
H2	3.457	H2	1.057	Ethane	1.045
		CO2	39.101	Others	15.848
		H2O	0.368	Total	18.234
		HCs	18.234	Product	H/C ratio
TOTAL IN	72.071	OUT	72.071		2.155
				O/C ratio	0.163
HC Yield	HCs	C1+C2(p	CO Conversion Rate, gmole/kg Fe/hr		
g/h/gFe	0.441	0.058	Syngas Converted, Nm ^3/hr/m ^3 Rx		
g/nL syn	0.195	0.026	STY of C3+ in 24 hrs, kg/m ^3 Rx		

TABLE 7
SUMMARY PERFORMANCE DATA FOR RUHRCHEMIE AND UCI CATALYSTS

CONDITIONS:

200 OR 290 PSIG
265°C

2.4 NI/hr/g Fe
H₂:CO (FEED) = 0.7

Catalyst	Run Number	Conversion, %		H ₂ :CO Usage Ratio	Selectivity, %			
		CO	CO+H ₂		C ₁	C ₂	C ₃ ¹	CO ₂
Ruhrchemie	31 ¹	70	68	0.70	4.0	1.8	1.9	43
UCI "O"	44 ¹	78	70	0.58	3.6	0.90	2.4	48
UCI "O"	48 ¹	70	65	0.62	5.4 ³	2.4	3.5	45
UCI "A"	50 ¹	70	65	0.56	2.7	0.75	2.2	46
UCI "B"	51 ¹	56	57	0.65	3.1 ⁴	1.8	2.8	45
Start-up	53 ¹	70	60	0.54	3.6	1.3	3.3	50
Composite	54 ²	80	75	0.55	3.2	0.6	2.3	47
1. 290 psig 2. 200 psig 3. Ultimate line-out selectivity = 6.5% 4. Ultimate line-out selectivity = 6.0%								

TABLE 8
MATERIAL BALANCE FOR RUN 50 AT 250 HOS

Run No: 50		HOS: 250		Catalyst:		UCI "A"	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole			
		Rx T, C	265				
Copper	2.00	K	538	Inlet, I	0.700		
Potassium	1.73	Rx P, psig	290	Outlet, O	0.850		
Silicon	2.99	kPa	2101	Usage, U	0.574		
Wt of catalyst in Rx, g		72.70	Conversion and Selectivity				
Wt of Fe in Rx, g		47.22	CO Conversion		54.0		
Wt % Fe in catalyst		64.95	H2 Conversion		44.3		
Wt of start-up oil, g		290.00	H2+CO Conversion		50.0		
Wt of Slurry, g		362.70	Selectivity to CO2		48.0		
Vol. of Slurry, cm ^3		458.69	Selectivity to CH4		2.9		
Wt % Solids in Rx		20.04	Selectivity to C2H6		0.9		
Solids Conc., g/cm ^3		0.1584945					
Syngas Feed Rate,		Material Balances, mol/hr					
nL/h/gFe	2.256		In	Out	Converted		
1E-5 mole/s/gFe	2.796	CO	2.796	1.286	1.510		
mol/hr	4.753	H2	1.957	1.090	0.867		
L/h/gFe	0.214	H2 + CO	4.753	2.376	2.376		
Water-Gas Shift Equilibrium Calculations							
Equm. Cons. K = [CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]							
K = 65.141		H2O out = 0.009		mol/hr			
mol/hr		Atomic Balance, mol/hr					
CO to CO2	0.725	C, in	2.796	H, in	3.914	O, in	2.796
CO to HC	0.785	Out	2.796	Out	3.914	Out	
CO to CH4	0.023	as CO2	0.725	as H2O	0.019	as H2O	0.009
CO to C2H6	0.014	as HC	0.785	as HC	1.715	as CO2	1.449
H2 to H2O	0.009	as CO	1.286	as H2	2.181	as CO	1.286
H2 to HC	0.857					as HCO	0.051
Mass Balance in g/hr				HCs Distribution, g/hr			
IN		OUT		Methane		0.365	
CO	78.313	CO	36.024	Ethane		0.212	
H2	3.945	H2	2.198	Others		11.395	
		CO2	31.893	Total		11.973	
		H2O	0.170				
		HCs	11.973				
TOTAL IN	82.258	OUT	82.258	Product H/C ratio		2.184	
				O/C ratio		0.065	
HC Yield	HCs	C1+C2(p	CO Conversion Rate, gmole/kg Fe/hr				32
g/h/gFe	0.254	0.012	Syngas Converted, Nm ^3/hr/m ^3 Rx				116
g/nL syn	0.112	0.005	STY of C3+ in 24 hrs, kg/m ^3 Rx				596

TABLE 9
MATERIAL BALANCE FOR RUN 51 AT 320 HOS

Run No: 51		HOS: 320		Catalyst:		UCI "B"	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole			
		Rx T, C		265			
Copper	1.34	K		538		Inlet, I	0.700
Potassium	1.32	Rx P, psig		290		Outlet, O	0.750
Silicon	4.23	kPa		2101		Usage, U	0.672
Wt of catalyst in Rx, g		72.70		Conversion and Selectivity			
Wt of Fe in Rx, g		46.82		CO Conversion		60.0	
Wt % Fe in catalyst		64.40		H2 Conversion		57.6	
Wt of start-up oil, g		290.00		H2+CO Conversion		59.0	
Wt of Slurry, g		362.70		Selectivity to CO2		47.6	
Vol. of Slurry, cm ^ 3		458.69		Selectivity to CH4		5.9	
Wt % Solids in Rx		20.04		Selectivity to C2H6		3.3	
Solids Conc., g/cm ^ 3		0.1584945					
Syngas Feed Rate,		Material Balances, mol/hr					
nL/h/gFe	2.256			In	Out	Converted	
1E-5 mole/s/gFe	2.796	CO		2.772	1.109	1.663	
mol/hr	4.712	H2		1.940	0.823	1.117	
L/h/gFe	0.214	H2 + CO		4.712	1.932	2.780	
Water-Gas Shift Equilibrium Calculations							
Equm. Cons. K =		[CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]					
K =		65.141		H2O out =		0.009 mol/hr	
mol/hr		Atomic Balance, mol/hr					
CO to CO2	0.792	C, in	2.772	H, in	3.881	O, in	2.772
CO to HC	0.871	Out	2.772	Out	3.881	Out	
CO to CH4	0.051	as CO2	0.792	as H2O	0.018	as H2O	0.009
CO to C2H6	0.058	as HC	0.871	as HC	2.216	as CO2	1.583
H2 to H2O	0.009	as CO	1.109	as H2	1.646	as CO	1.109
H2 to HC	1.108					as HCO	0.071
Mass Balance in g/hr				HCs Distribution, g/hr			
IN		OUT		Methane		0.825	
CO	77.641	CO	31.056	Ethane		0.865	
H2	3.912	H2	1.660	Others		12.144	
		CO2	34.840	Total		13.834	
		H2O	0.163				
		HCs	13.834				
TOTAL IN	81.552	OUT	81.552	Product H/C ratio		2.543	
				O/C ratio		0.081	
HC Yield	HCs	C1+C2(p	CO Conversion Rate, gmole/kg Fe/hr		36		
g/h/gFe	0.295	0.036	Syngas Converted, Nm ^ 3/hr/m ^ 3 Rx		136		
g/nL syn	0.131	0.016	STY of C3+ in 24 hrs, kg/m ^ 3 Rx		635		

TABLE 10
MATERIAL BALANCE FOR RUN 53 AT 140 HOS

Run No: 53		HOS: 140		Catalyst:		UCI "START-UP"		
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole				
		Rx T, C	265					
Copper	7.52	K	538	Inlet, I	0.700			
Potassium	2.57	Rx P, psig	200	Outlet, O	0.770			
Silicon	4.29	kPa	1480	Usage, U	0.621			
Wt of catalyst in Rx, g		72.70		Conversion and Selectivity				
Wt of Fe in Rx, g		44.15		CO Conversion		49.5		
Wt % Fe in catalyst		60.73		H2 Conversion		43.9		
Wt of start-up oil, g		290.00		H2+CO Conversion		47.2		
Wt of Slurry, g		362.70		Selectivity to CO2		49.0		
Vol. of Slurry, cm ^ 3		458.69		Selectivity to CH4		3.8		
Wt % Solids in Rx		20.04		Selectivity to C2H6		1.2		
Solids Conc., g/cm ^ 3		0.1584945						
Syngas Feed Rate,		Material Balances, mol/hr						
nL/h/gFe	2.256			In	Out	Converted		
1E-5 mole/s/gFe	2.796	CO		2.614	1.320	1.294		
mol/hr	4.444	H2		1.830	1.026	0.804		
L/h/gFe	0.304	H2 + CO		4.444	2.346	2.098		
Water-Gas Shift Equilibrium Calculations								
Equm. Cons. K =		[CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]						
K =		65.141		H2O out =		0.008 mol/hr		
mol/hr		Atomic Balance, mol/hr						
CO to CO2	0.634	C, in	2.614	H, in	3.660	O, in	2.614	
CO to HC	0.660	Out	2.614	Out	3.660	Out		
CO to CH4	0.025	as CO2	0.634	as H2O	0.015	as H2O	0.008	
CO to C2H6	0.016	as HC	0.660	as HC	1.592	as CO2	1.268	
H2 to H2O	0.008	as CO	1.320	as H2	2.053	as CO	1.320	
H2 to HC	0.796					as HCO	0.018	
Mass Balance in g/hr				HCs Distribution, g/hr				
	IN		OUT	Methane		0.402		
CO	73.222	CO	36.977	Ethane		0.238		
H2	3.689	H2	2.069	Others		9.184		
		CO2	27.905	Total		9.824		
		H2O	0.136					
		HCs	9.824					
TOTAL IN	76.911	OUT	76.911	Product H/C ratio		2.412		
				O/C ratio		0.028		
HC Yield	HCs	C1+C2(p	CO Conversion Rate, gmole/kg Fe/hr					29
g/h/gFe	0.223	0.015	Syngas Converted, Nm ^ 3/hr/m ^ 3 Rx					102
g/nL syn	0.099	0.006	STY of C3+ in 24 hrs, kg/m ^ 3 Rx					481

TABLE 11
MATERIAL BALANCE FOR RUN 53 AT 220 HOS

Run No: 53		HOS: 220		Catalyst: UCI "START-UP"	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole	
		Rx T, C	265	Inlet, I	0.700
Copper	7.52	K	538	Outlet, O	0.820
Potassium	2.57	Rx P, psig	400	Usage, U	0.573
Silicon	4.29	kPa	2859		
Wt of catalyst in Rx, g			72.70	Conversion and Selectivity	
Wt of Fe in Rx, g			44.15	CO Conversion	48.0
Wt % Fe in catalyst			60.73	H2 Conversion	39.3
Wt of start-up oil, g			290.00	H2+CO Conversion	44.4
Wt of Slurry, g			362.70	Selectivity to CO2	47.0
Vol. of Slurry, cm ^3			458.69	Selectivity to CH4	2.9
Wt % Solids in Rx			20.04	Selectivity to C2H6	0.6
Solids Conc., g/cm ^3			0.1584945		
Syngas Feed Rate,		Material Balances, mol/hr			
nL/h/gFe	4.700		In	Out	Converted
1E-5 mole/s/gFe	5.825	CO	5.446	2.832	2.614
mol/hr	9.258	H2	3.812	2.316	1.497
L/h/gFe	0.328	H2 + CO	9.258	5.148	4.111
Water-Gas Shift Equilibrium Calculations					
Equm. Cons. K = $\frac{[CO_2][H_2]}{[CO][H_2O]} = \exp[4577.8/T-4.33]$					
K = 65.141		H2O out = 0.015 mol/hr			
mol/hr		Atomic Balance, mol/hr			
CO to CO2	1.229	C, in	5.446	H, in	7.625
CO to HC	1.385	Out	5.446	Out	7.625
CO to CH4	0.040	as CO2	1.229	as H2O	0.031
CO to C2H6	0.017	as HC	1.385	as HC	2.962
H2 to H2O	0.015	as CO	2.832	as H2	4.631
H2 to HC	1.481			as HCO	0.141
Mass Balance in g/hr			HCs Distribution, g/hr		
IN		OUT		Methane	0.645
CO	152.547	CO	79.324	Ethane	0.250
H2	7.686	H2	4.668	Others	20.995
		CO2	54.072	Total	21.890
		H2O	0.278		
		HCs	21.890	Product H/C ratio	2.138
TOTAL IN	160.232	OUT	160.232	O/C ratio	0.102
HC Yield	HCs	C1+C2(p)	CO Conversion Rate, gmole/kg Fe/hr		
g/h/gFe	0.496	0.020	Syngas Converted, Nm ^3/hr/m ^3 Rx		
g/nL syn	0.105	0.004	STY of C3+ in 24 hrs, kg/m ^3 Rx		

TABLE 12
MATERIAL BALANCE FOR RUN 53 AT 360 HOS

Run No: 53		HOS: 360		Catalyst:		UCI "START-UP"	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole			
		Rx T, C 265					
Copper	7.52	K 538		Inlet, I		0.700	
Potassium	2.57	Rx P, psig 290		Outlet, O		0.800	
Silicon	4.29	kPa 2101		Usage, U		0.630	
Wt of catalyst in Rx, g		72.70		Conversion and Selectivity			
Wt of Fe in Rx, g		44.15		CO Conversion		61.0	
Wt % Fe in catalyst		60.73		H2 Conversion		54.9	
Wt of start-up oil, g		290.00		H2+CO Conversion		58.5	
Wt of Slurry, g		362.70		Selectivity to CO2		48.0	
Vol. of Slurry, cm ^ 3		458.69		Selectivity to CH4		3.0	
Wt % Solids in Rx		20.04		Selectivity to C2H6		0.7	
Solids Conc., g/cm ^ 3		0.1584945					
Syngas Feed Rate,		Material Balances, mol/hr					
nL/h/gFe	2.256			In	Out	Converted	
1E-5 mole/s/gFe	2.796	CO		2.614	1.020	1.595	
mol/hr	4.444	H2		1.830	0.825	1.005	
L/h/gFe	0.214	H2 + CO		4.444	1.844	2.600	
Water-Gas Shift Equilibrium Calculations							
Equm. Cons. K = [CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]							
K = 65.141		H2O out = 0.010		mol/hr			
mol/hr		Atomic Balance, mol/hr					
CO to CO2	0.765	C, in	2.614	H, in	3.660	O, in	2.614
CO to HC	0.829	Out	2.614	Out	3.660	Out	
CO to CH4	0.025	as CO2	0.765	as H2O	0.019	as H2O	0.010
CO to C2H6	0.012	as HC	0.829	as HC	1.991	as CO2	1.531
H2 to H2O	0.010	as CO	1.020	as H2	1.650	as CO	1.020
H2 to HC	0.996					as HCO	0.054
Mass Balance in g/hr				HCs Distribution, g/hr			
IN		OUT		Methane		0.399	
CO	73.222	CO	28.557	Ethane		0.175	
H2	3.689	H2	1.663	Others		12.261	
		CO2	33.686	Total		12.835	
		H2O	0.171				
		HCs	12.835	Product H/C ratio		2.401	
TOTAL IN	76.911	OUT	76.911	O/C ratio		0.065	
HC Yield	HCs	C1+C2(p	CO Conversion Rate, gmole/kg Fe/hr		36		
g/h/gFe	0.291	0.013	Syngas Converted, Nm ^ 3/hr/m ^ 3 Rx		127		
g/nL syn	0.129	0.006	STY of C3+ in 24 hrs, kg/m ^ 3 Rx		642		

TABLE 13
MATERIAL BALANCE FOR RUN 54 AT 175 HOS

Run No: 54		HOS: 175		Catalyst:		UCI "COMPOSITE"	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole			
		Rx T, C		265			
Copper	7.86	K		538		Inlet, I	0.700
Potassium	7.86	Rx P, psig		200		Outlet, O	1.250
Silicon	11.02	kPa		1480		Usage, U	0.559
Wt of catalyst in Rx, g		72.70		Conversion and Selectivity			
Wt of Fe in Rx, g		39.12		CO Conversion		79.6	
Wt % Fe in catalyst		53.81		H2 Conversion		63.6	
Wt of start-up oil, g		290.00		H2+CO Conversion		73.0	
Wt of Slurry, g		362.70		Selectivity to CO2		47.0	
Vol. of Slurry, cm ^3		458.69		Selectivity to CH4		3.5	
Wt % Solids in Rx		20.04		Selectivity to C2H6		0.7	
Solids Conc., g/cm ^3		0.1584945					
Syngas Feed Rate,		Material Balances, mol/hr					
nL/h/gFe	2.322			In	Out	Converted	
1E-5 mole/s/gFe	2.877	CO		2.384	0.486	1.897	
mol/hr	4.052	H2		1.668	0.608	1.061	
L/h/gFe	0.313	H2 + CO		4.052	1.094	2.958	
Water-Gas Shift Equilibrium Calculations							
Equm. Cons. K =		$[CO_2][H_2]/[CO][H_2O] = \exp[4577.8/T-4.33]$					
K =		65.141		H2O out =		0.017 mol/hr	
mol/hr		Atomic Balance, mol/hr					
CO to CO2	0.892	C, in	2.384	H, in	3.337	O, in	2.384
CO to HC	1.006	Out	2.384	Out	3.337	Out	
CO to CH4	0.035	as CO2	0.892	as H2O	0.034	as H2O	0.017
CO to C2H6	0.014	as HC	1.006	as HC	2.087	as CO2	1.783
H2 to H2O	0.017	as CO	0.486	as H2	1.216	as CO	0.486
H2 to HC	1.044					as HCO	0.097
Mass Balance In g/hr				HCs Distribution, g/hr			
IN		OUT		Methane		0.565	
CO	66.764	CO	13.620	Ethane		0.212	
H2	3.364	H2	1.225	Others		14.953	
		CO2	39.245	Total		15.729	
		H2O	0.308				
		HCs	15.729				
TOTAL IN	70.128	OUT	70.128	Product H/C ratio		2.076	
				O/C ratio		0.096	
HC Yield	HCs	C1+C2(p	CO Conversion Rate, gmole/kg Fe/hr		49		
g/h/gFe	0.402	0.020	Syngas Converted, Nm ^3/hr/m ^3 Rx		144		
g/nL syn	0.173	0.009	STY of C3+ in 24 hrs, kg/m ^3 Rx		782		

TABLE 14
MATERIAL BALANCE FOR RUN 54 AT 240 HOS

Run No: 54		HOS: 240		Catalyst:		UCI "COMPOSITE"	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole			
		Rx T, C 265		Inlet, I 0.700		Outlet, O 0.750	
Copper	7.86	K 538		Usage, U 0.640			
Potassium	7.86	Rx P, psig 200					
Silicon	11.02	kPa 1480					
Wt of catalyst in Rx, g		65.70		Conversion and Selectivity			
Wt of Fe in Rx, g		35.35		CO Conversion		45.0	
Wt % Fe in catalyst		53.81		H2 Conversion		41.1	
Wt of start-up oil, g		290.00		H2+CO Conversion		43.4	
Wt of Slurry, g		355.70		Selectivity to CO2		48.0	
Vol. of Slurry, cm ^ 3		456.43		Selectivity to CH4		3.9	
Wt % Solids in Rx		18.47		Selectivity to C2H6		0.2	
Solids Conc., g/cm ^ 3		0.1439423					
Syngas Feed Rate,		Material Balances, mol/hr					
nL/h/gFe	5.201			In	Out	Converted	
1E-5 mole/s/gFe	6.445	CO		4.825	2.654	2.171	
mol/hr	8.202	H2		3.377	1.989	1.389	
L/h/gFe	0.701	H2 + CO		8.202	4.643	3.560	
Water-Gas Shift Equilibrium Calculations							
Equm. Cons. K = [CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]							
K = 65.141		H2O out = 0.012		mol/hr			
mol/hr		Atomic Balance, mol/hr					
CO to CO2	1.042	C, in	4.825	H, in	6.755	O, in	4.825
CO to HC	1.129	Out	4.825	Out	6.755	Out	
CO to CH4	0.044	as CO2	1.042	as H2O	0.024	as H2O	0.012
CO to C2H6	0.005	as HC	1.129	as HC	2.753	as CO2	2.084
H2 to H2O	0.012	as CO	2.654	as H2	3.978	as CO	2.654
H2 to HC	1.377					as HCO	0.075
Mass Balance in g/hr				HCs Distribution, g/hr			
IN		OUT		Methane		0.706	
CO	135.150	CO	74.332	Ethane		0.068	
H2	6.809	H2	4.010	Others		16.760	
		CO2	45.867	Total		17.534	
		H2O	0.216				
		HCs	17.534	Product H/C ratio		2.439	
TOTAL IN	141.959	OUT	141.959	O/C ratio		0.066	
HC Yield	HCs	C1+C2(p)	CO Conversion Rate, gmole/kg Fe/hr		61		
g/h/gFe	0.496	0.022	Syngas Converted, Nm ^ 3/hr/m ^ 3 Rx		175		
g/nL syn	0.095	0.004	STY of C3+ in 24 hrs, kg/m ^ 3 Rx		881		

TABLE 15
MATERIAL BALANCE FOR RUN 54 AT 360 HOS

Run No: 54		HOS: 360		Catalyst:		UCI "COMPOSITE"	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole			
		Rx T, C 265		Inlet, I 0.700		Outlet, O 0.780	
Copper	7.86	K 538		Usage, U 0.631			
Potassium	7.86	Rx P, psig 400					
Silicon	11.02	kPa 2859					
Wt of catalyst in Rx, g		61.15		Conversion and Selectivity			
Wt of Fe in Rx, g		32.90		CO Conversion		54.2	
Wt % Fe in catalyst		53.81		H2 Conversion		48.9	
Wt of start-up oil, g		290.00		H2+CO Conversion		52.0	
Wt of Slurry, g		351.15		Selectivity to CO2		37.5	
Vol. of Slurry, cm ^3		454.97		Selectivity to CH4		2.6	
Wt % Solids in Rx		17.41		Selectivity to C2H6		0.5	
Solids Conc., g/cm ^3		0.1344059					
Syngas Feed Rate,		Material Balances, mol/hr					
nL/h/gFe	2.626			In	Out	Converted	
1E-5 mole/s/gFe	3.255	CO		2.268	1.039	1.229	
mol/hr	3.855	H2		1.587	0.812	0.776	
L/h/gFe	0.183	H2 + CO		3.855	1.850	2.005	
Water-Gas Shift Equilibrium Calculations							
Equm. Cons. K = [CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]							
K =		65.141		H2O out =		0.006 mol/hr	
mol/hr		Atomic Balance, mol/hr					
CO to CO2	0.461	C, in	2.268	H, in	3.175	O, in	2.268
CO to HC	0.768	Out	2.268	Out	3.175	Out	
CO to CH4	0.020	as CO2	0.461	as H2O	0.011	as H2O	0.006
CO to C2H6	0.008	as HC	0.768	as HC	1.540	as CO2	0.922
H2 to H2O	0.006	as CO	1.039	as H2	1.624	as CO	1.039
H2 to HC	0.770					as HCO	0.302
Mass Balance In g/hr				HCs Distribution, g/hr			
IN		OUT		Methane		0.320	
CO	63.520	CO	29.092	Ethane		0.115	
H2	3.200	H2	1.637	Others		15.171	
		CO2	20.285	Total		15.607	
		H2O	0.100				
		HCs	15.607	Product H/C ratio		2.005	
TOTAL IN	66.721	OUT	66.721	O/C ratio		0.393	
HC Yield	HCs	C1+C2(p	CO Conversion Rate, gmole/kg Fe/hr		37		
g/h/gFe	0.474	0.013	Syngas Converted, Nm ^3/hr/m ^3 Rx		99		
g/nL syn	0.181	0.005	STY of C3+ in 24 hrs, kg/m ^3 Rx		800		

TABLE 16
MATERIAL BALANCE FOR RUN 54 AT 500 HOS

Run No: 54		HOS: 500		Catalyst:		UCI "COMPOSITE"	
Catalyst Composition, g/100 g Fe		Operating Conditions		H2/CO Ratios, mole/mole			
		Rx T, C		265			
Copper	7.86	K		538		Inlet, I	0.700
Potassium	7.86	Rx P, psig		200		Outlet, O	0.770
Silicon	11.02	kPa		1480		Usage, U	0.604
Wt of catalyst in Rx, g		61.15		Conversion and Selectivity			
Wt of Fe in Rx, g		32.90		CO Conversion		42.4	
Wt % Fe in catalyst		53.81		H2 Conversion		36.6	
Wt of start-up oil, g		290.00		H2+CO Conversion		40.0	
Wt of Slurry, g		351.15		Selectivity to CO2		44.0	
Vol. of Slurry, cm ^3		454.97		Selectivity to CH4		3.9	
Wt % Solids in Rx		17.41		Selectivity to C2H6		0.6	
Solids Conc., g/cm ^3		0.1344059					
Syngas Feed Rate,		Material Balances, mol/hr					
nL/h/gFe	2.794			In	Out	Converted	
1E-5 mole/s/gFe	3.463	CO		2.412	1.390	1.023	
mol/hr	4.101	H2		1.689	1.071	0.618	
L/h/gFe	0.377	H2 + CO		4.101	2.461	1.640	
Water-Gas Shift Equilibrium Calculations							
Eqm. Cons. K =		[CO2][H2]/[CO][H2O] = exp[4577.8/T-4.33]					
K =		65.141		H2O out =		0.005 mol/hr	
mol/hr		Atomic Balance, mol/hr					
CO to CO2	0.450	C, in	2.412	H, in	3.377	O, in	2.412
CO to HC	0.573	Out	2.412	Out	3.377	Out	
CO to CH4	0.022	as CO2	0.450	as H2O	0.011	as H2O	0.005
CO to C2H6	0.007	as HC	0.573	as HC	1.225	as CO2	0.900
H2 to H2O	0.005	as CO	1.390	as H2	2.142	as CO	1.390
H2 to HC	0.612					as HCO	0.117
Mass Balance in g/hr				HCs Distribution, g/hr			
IN		OUT		Methane		0.358	
CO	67.575	CO	38.923	Ethane		0.103	
H2	3.405	H2	2.159	Others		9.531	
		CO2	19.808	Total		9.993	
		H2O	0.096				
		HCs	9.993	Product H/C ratio		2.138	
TOTAL IN	70.979	OUT	70.979	O/C ratio		0.205	
HC Yield	HCs	C1+C2(p)	CO Conversion Rate, gmole/kg Fe/hr		31		
g/h/gFe	0.304	0.014	Syngas Converted, Nm ^3/hr/m ^3 Rx		81		
g/nL syn	0.109	0.005	STY of C3+ in 24 hrs, kg/m ^3 Rx		503		

Run No.: **54** HOS: **175**
Catalyst: **UCI "COMPOSITE"**

Alpha	-0.500
Alpha*	-0.574
Da	3.090
Henry's Constant, Pa*m ^ 3/mol	25979
Rate Parameter, kp 1E-11 mol/s/g Fe/Pa	6.01
Reaction Rate, -r(CO+H2) 1E-5 mol/s/gFe	2.10
1E-5 mol/s	82.17
Rate Constant, 1E-3 m ^ 3/kg Fe/s	0.5596

TABLE 18
KINETIC PARAMETERS FROM RUN 54 (240 HOS)

240

UCI "COMPOSITE"

Catalyst Composition, g/100 g Fe		Operating Conditions	
Copper	7.86	Reactor T, C	265
Potassium	7.86	K	538
Silicon	11.02	Reactor P, psig	200
		kPa	1480
Wt of catalyst, g	65.70	Syngas Feed Rate,	
Wt of Fe in Rx, g	35.35	nL/h/gFe	5.201
Wt % Fe in catalyst	53.81	1E-5 mole/s/gFe	6.445
Wt of start-up oil, g	290.00	mol/hr	8.202
Volume of Slurry, cm ³	456.43	L/h/gFe	0.701
Wt % Solids in Rx	18.47		
Volume % Solids in Rx	4.64		
H ₂ /CO Ratios, mole/mole		Conversion and Selectivity	
Inlet, I	0.700	CO Conversion	45.0
Outlet, O	0.750	H ₂ Conversion	41.1
Usage, U	0.640	H ₂ + CO Conversion	43.4
		Selectivity to CO ₂	48.0
		Selectivity to CH ₄	3.9
		Selectivity to C ₂ H ₆	0.2

Alpha	-0.500
Alpha*	-0.528
Da	1.401
Henry's Constant, Pa*m ^ 3/mol	25979
Rate Parameter, kp 1E-11 mol/s/g Fe/Pa	6.10
Reaction Rate, -r(CO+H2) 1E-5 mol/s/gFe	2.80
1E-5 mol/s	98.89
Rate Constant, 1E-3 m ^ 3/kg Fe/s	0.6184

Run No.: 54 HOS: 360
Catalyst: UCI "COMPOSITE"

Alpha	-0.500
Alpha*	-0.532
Da	1.827
Henry's Constant, Pa*m ^ 3/mol	25979
Rate Parameter, kp 1E-11 mol/s/g Fe/Pa	4.43
Reaction Rate, -r(CO+H2) 1E-5 mol/s/gFe	3.60
1E-5 mol/s	118.48
Rate Constant, 1E-3 m ^ 3/kg Fe/s	0.4448

TABLE 20
KINETIC PARAMETERS FROM RUN 54 (500 HOS)

Run No.: 54

HOS: 500

Catalyst:

UCI "COMPOSITE"

Catalyst Composition, g/100 g Fe		Operating Conditions	
		Reactor T, C	265
Copper	7.86	K	538
Potassium	7.86	Reactor P, psig	200
Silicon	11.02	kPa	1480
Wt of catalyst, g	61.15	Syngas Feed Rate,	
Wt of Fe in Rx, g	32.90	nL/h/gFe	2.794
Wt % Fe in catalyst	53.81	1E-5 mole/s/gFe	3.463
Wt of start-up oil, g	290.00	mol/hr	4.101
Volume of Slurry, cm ³	454.97	L/h/gFe	0.377
Wt % Solids in Rx	17.41		
Volume % Solids in Rx	4.34		
H ₂ /CO Ratios, mole/mole		Conversion and Selectivity	
		CO Conversion	42.4
Inlet, I	0.700	H ₂ Conversion	36.6
Outlet, O	0.770	H ₂ +CO Conversion	40.0
Usage, U	0.604	Selectivity to CO ₂	44.0
		Selectivity to CH ₄	3.9
		Selectivity to C ₂ H ₆	0.6

Alpha	-0.500
Alpha*	-0.547
Da	1.225
Henry's Constant, Pa*m ³ /mol	25979
Rate Parameter, kp 1E-11 mol/s/g Fe/Pa	2.87
Reaction Rate, -r(CO+H ₂) 1E-5 mol/s/gFe	1.39
1E-5 mol/s	45.57
Rate Constant, 1E-3 m ³ /kg Fe/s	0.2803

TABLE 21
COMPARISON WITH LAPORTE SBCR RUN AF-R6.1A

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	16.6	83.4	100
Density, g/cm ³	3.100	0.666	0.766
Volume % Solids	4.10	95.90	100.00
Viscosity, g/cm/s	-	0.0225	0.0308
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.40
Catalyst Weight, kg	178.6
Cat. Loading, kg/m ³	127.2

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	4.0
Feed Rate, am ³ /hr	36.6
nm ³ /hr	271.3
SV, am ³ /hr/m ³	26.1
nm ³ /hr/m ³	193.2
nm ³ /h/kg Fe	2.82
Corr. factor for kLa	0.587
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.1-A		
	Plant	MODEL 1	MODEL 2
H2 Conversion, %	61.9	60.5	57.0
Ug, cm/sec		2.6	2.7
Gas hold-up, eps-g	0.15	0.101	0.103
kLa (uncorr), 1/s		0.287	0.292
kLa (corr), 1/s		0.168	0.171
kr. epsl, 1/s		0.038	0.038
KR(=kr. epsl.R.T/He)		0.007	0.007
KM(=kLa.R.T/He)		0.029	0.029
K(=KR.KM/(KR+KM))		0.005	0.005
H2+CO Conversion, %	72.4	69.5	65.5
CO Conversion, %	80.2	75.8	71.4
STY, nm ³ /h/m ³		134.2	126.5
STY, nm ³ /h/kg Fe		1.96	1.85
Mass Transfer Res., %		18.55	18.27
CO Conv., gmole/kg Fe/h	55.3	56.14	52.91
-CH2 produced, g/kg Fe/h		417.35	393.38
g/nm ³ syngas		147.80	139.32

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 22
COMPARISON WITH LAPORTE SBGR RUN AF-R6.1B

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	16.2	83.8	100
Density, g/cm ³	3.100	0.866	0.783
Volume % Solids	3.99	96.01	100.00
Viscosity, g/cm/s	-	0.0225	0.0305
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	608.6
Slurry Level, fraction	0.88
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.37
Catalyst Weight, kg	169.6
Cat. Loading, kg/m ³	123.7

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	4.0
Feed Rate, am ³ /hr	36.6
nm ³ /hr	271.3
SV, am ³ /hr/m ³	26.7
nm ³ /hr/m ³	197.9
nm ³ /h/kg Fe	2.97
Corr. factor for kLa	0.589
H ₂ Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.1-B		
	Plant	MODEL 1	MODEL 2
H ₂ Conversion, %	60.8	58.5	55.4
U _g , cm/sec		2.6	2.7
Gas hold-up, eps-g	0.15	0.102	0.104
kLa (uncorr), 1/s		0.289	0.294
kLa (corr), 1/s		0.170	0.173
kr.epsl, 1/s		0.037	0.037
KR(=kr.epsl.R.T/He)		0.006	0.006
KM(=kLa.R.T/He)		0.029	0.030
K(=KR.KM/(KR+KM))		0.005	0.005
H ₂ +CO Conversion, %	68.4	67.2	63.7
CO Conversion, %	73.8	73.2	69.4
STY, nm ³ /h/m ³		132.9	126.0
STY, nm ³ /h/kg Fe		2.00	1.89
Mass Transfer Res., %		17.83	17.70
CO Conv., gmole/kg Fe/h	55.9	57.16	54.17
-CH ₂ produced, g/kg Fe/h		424.94	402.73
g/nm ³ syngas		142.92	135.45

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 23
COMPARISON WITH LAPORTE SBCR RUN AF-R6.1C

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	15.43	84.57	100
Density, g/cm ³	3.100	0.866	0.758
Volume % Solids	3.77	96.23	100.00
Viscosity, g/cm/s	-	0.0225	0.0300
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	164.6
Cat. Loading, kg/m ³	117.0

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	4.0
Feed Rate, m ³ /hr	36.6
nm ³ /hr	271.3
SV, m ³ /hr/m ³	26.0
nm ³ /hr/m ³	192.8
nm ³ /h/kg Fe	3.06
Corr. factor for kLa	0.593
H ₂ Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.1-C		
	Plant	MODEL 1	MODEL 2
H ₂ Conversion, %	53.0	57.7	54.6
U _g , cm/sec		2.7	2.7
Gas hold-up, eps-g	0.134	0.103	0.104
kLa (uncorr), 1/s		0.290	0.295
kLa (corr), 1/s		0.172	0.175
kr,eps, 1/s		0.035	0.035
KR(=kr,eps, R.T./He)		0.006	0.006
KM(=kL, a.R.T./He)		0.030	0.030
K(=KR.KM/(KR+KM))		0.005	0.005
H ₂ +CO Conversion, %	58.7	66.2	62.7
CO Conversion, %	62.7	72.2	68.4
STY, nm ³ /h/m ³		127.7	120.9
STY, nm ³ /h/kg Fe		2.03	1.92
Mass Transfer Res., %		16.99	16.77
CO Conv., gmole/kg Fe/h	49.1	58.04	54.98
CH ₂ produced, g/kg Fe/h		431.47	408.76
g/nm ³ syngas		140.86	133.45

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 24
COMPARISON WITH LAPORTE SBGR RUN AF-R6.1D

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	14.35	85.65	100
Density, g/cm ³	3.100	0.688	0.751
Volume % Solids	3.48	96.52	100.00
Viscosity, g/cm/s	-	0.0225	0.0293
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	809.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	151.7
Cat. Loading, kg/m ³	107.8

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	3.7
Feed Rate, am ³ /hr	33.8
nm ³ /hr	250.5
SV, am ³ /hr/m ³	24.0
nm ³ /hr/m ³	178.0
nm ³ /h/kg Fe	3.07
Corr. factor for kLa	0.597
H ₂ Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.1-D		
	Plant	MODEL 1	MODEL 2
H ₂ Conversion, %	54.7	57.8	54.8
U _g , cm/sec		2.4	2.5
Gas hold-up, eps-g	0.121	0.098	0.099
kLa (uncorr), 1/s		0.276	0.280
kLa (corr), 1/s		0.165	0.168
kr, epsl, 1/s		0.032	0.032
KR(=kr, epsl, R.T./He)		0.006	0.006
KM(=kLa, R.T./He)		0.028	0.029
K(=KR.KM/(KR+KM))		0.005	0.005
H ₂ +CO Conversion, %	60.7	66.4	62.7
CO Conversion, %	65.0	72.4	68.4
STY, nm ³ /h/m ³		118.2	111.7
STY, nm ³ /h/kg Fe		2.04	1.93
Mass Transfer Res., %		16.45	16.23
CO Conv., gmole/kg Fe/h	50.8	58.34	55.11
CH ₂ produced, g/kg Fe/h		433.74	409.72
g/nm ³ syngas		141.30	133.48

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 25
COMPARISON WITH LAPORTE SBCR RUN AF-R6.1E

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	14.03	85.97	100
Density, g/cm ³	3.100	0.866	0.749
Volume % Solids	3.39	96.61	100.00
Viscosity, g/cm/s	-	0.0225	0.0291
Surface Tension, N/m	-	18.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	809.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	147.9
Cat. Loading, kg/m ³	105.1

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	4.3
Feed Rate, am ³ /hr	39.4
nm ³ /hr	292.2
SV, am ³ /hr/m ³	28.0
nm ³ /hr/m ³	207.6
nm ³ /h/kg Fe	3.67
Corr. factor for kLa	0.599
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.1-E		
	Plant	MODEL 1	MODEL 2
H2 Conversion, %	46.0	51.2	49.1
Ug, cm/sec		3.0	3.1
Gas hold-up, eps-g	0.137	0.110	0.111
kLa (uncorr), 1/s		0.314	0.317
kLa (corr), 1/s		0.188	0.190
kr,eps1, 1/s		0.032	0.032
KR(=kr,eps1.R.T/He)		0.005	0.005
KM(=kLa.R.T/He)		0.032	0.033
K(=KR.KM/(KR+KM))		0.005	0.005
H2+CO Conversion, %	50.5	58.8	56.4
CO Conversion, %	53.7	64.1	61.5
STY, nm ³ /h/m ³		122.1	117.0
STY, nm ³ /h/kg Fe		2.16	2.07
Mass Transfer Res., %		14.42	14.29
CO Conv., gmole/kg Fe/h	50.5	61.80	59.24
-CH2 produced, g/kg Fe/h		459.45	440.45
g/nm ³ syngas		125.08	119.91

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 26
COMPARISON WITH LAPORTE SBCR RUN AF-R6.1F

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	12.4	87.6	100
Density, g/cm ³	3.100	0.666	0.738
Volume % Solids	2.95	97.05	100.00
Viscosity, g/cm/s	-	0.0225	0.0282
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	606.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	128.8
Cat. Loading, kg/m ³	91.5

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	4.0
Feed Rate, am ³ /hr	36.6
nm ³ /hr	271.3
SV, am ³ /hr/m ³	26.0
nm ³ /hr/m ³	192.8
nm ³ /h/kg Fe	3.91
Corr. factor for kLa	0.605
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.1-F		
	Plant	MODEL 1	MODEL 2
H2 Conversion, %	45.4	49.2	47.2
Ug, cm/sec		2.8	2.9
Gas hold-up, eps-g	0.136	0.106	0.107
kLa (uncorr), 1/s		0.302	0.305
kLa (corr), 1/s		0.183	0.184
kr. epsl, 1/s		0.028	0.028
KR(=kr. epsl.R.T/He)		0.005	0.005
KM(=kLa.R.T/He)		0.031	0.032
K(=KR.KM/(KR+KM))		0.004	0.004
H2+CO Conversion, %	49.6	56.5	54.2
CO Conversion, %	52.5	61.6	59.1
STY, nm ³ /h/m ³		108.9	104.5
STY, nm ³ /h/kg Fe		2.21	2.12
Mass Transfer Res., %		13.11	13.00
CO Conv., gmole/kg Fe/h	52.7	63.29	60.71
CH2 produced, g/kg Fe/h		470.53	451.36
g/nm ³ syngas		120.20	115.30

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 27
COMPARISON WITH LAPORTE SBCR RUN AF-R6.1G

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	12.45	87.55	100
Density, g/cm ³	3.100	0.868	0.739
Volume % Solids	2.97	97.03	100.00
Viscosity, g/cm/s	-	0.0225	0.0282
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	129.4
Cat. Loading, kg/m ³	91.9

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	4.3
Feed Rate, am ³ /hr	39.4
nm ³ /hr	292.2
SV, am ³ /hr/m ³	28.0
nm ³ /hr/m ³	207.6
nm ³ /h/kg Fe	4.20
Corr. factor for kLa	0.605
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.1-G		
	Model	MODEL 1	MODEL 2
H2 Conversion, %	41.6	46.7	45.1
Ug, cm/sec		3.1	3.2
Gas hold-up, eps-g	0.137	0.112	0.113
kLa (uncorr), 1/s		0.320	0.323
kLa (corr), 1/s		0.193	0.195
kr,eps1, 1/s		0.028	0.028
KR(=kr,eps1.R.T/He)		0.005	0.005
KM(=kLa.R.T/He)		0.033	0.034
K(=KR.KM/(KR+KM))		0.004	0.004
H2+CO Conversion, %	44.5	53.6	51.7
CO Conversion, %	46.6	58.5	56.4
STY, nm ³ /h/m ³		111.3	107.4
STY, nm ³ /h/kg Fe		2.25	2.17
Mass Transfer Res., %		12.52	12.43
CO Conv., gmole/kg Fe/h	50.0	64.41	62.14
-CH2 produced, g/kg Fe/h		478.84	462.00
g/nm ³ syngas		114.09	110.08

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 28
COMPARISON WITH LAPORTE SBCR RUN AF-R6.1H

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	11.6	88.4	100
Density, g/cm ³	3.100	0.888	0.733
Volume % Solids	2.74	97.26	100.00
Viscosity, g/cm/s	-	0.0225	0.0277
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	119.7
Cat. Loading, kg/m ³	85.0

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	4.3
Feed Rate, am ³ /hr	39.4
nm ³ /hr	292.2
SV, am ³ /hr/m ³	28.0
nm ³ /hr/m ³	207.6
nm ³ /h/kg Fe	4.54
Corr. factor for kLa	0.607
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.1-H		
	Plant	MODEL 1	MODEL 2
H2 Conversion, %	38.4	44.2	42.7
Ug, cm/sec		3.2	3.2
Gas hold-up, eps-g	0.143	0.113	0.114
kLa (uncorr), 1/s		0.323	0.326
kLa (corr), 1/s		0.196	0.198
kr, epsl, 1/s		0.026	0.026
KR(=kr, epsl, R.T./He)		0.004	0.004
KM(=kLa, R.T./He)		0.034	0.034
K(=KR.KM/(KR+KM))		0.004	0.004
H2+CO Conversion, %	40.9	50.8	49.1
CO Conversion, %	42.5	55.3	53.5
STY, nm ³ /h/m ³		105.4	101.9
STY, nm ³ /h/kg Fe		2.30	2.23
Mass Transfer Res., %		11.53	11.46
CO Conv., gmole/kg Fe/h	49.5	65.91	63.72
-CH2 produced, g/kg Fe/h		490.01	473.73
g/nm ³ syngas		107.98	104.39

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 29
COMPARISON WITH LAPORTE SBCR RUN AF-R6.2A

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	10.49	89.51	100
Density, g/cm ³	3.100	0.666	0.726
Volume % Solids	2.46	97.54	100.00
Viscosity, g/cm/s	-	0.0225	0.0271
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	107.2
Cat. Loading, kg/m ³	76.2

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	8.2
Feed Rate, am ³ /hr	76.0
nm ³ /hr	563.6
SV, am ³ /hr/m ³	54.0
nm ³ /hr/m ³	400.4
nm ³ /h/kg Fe	9.77
Corr. factor for kLa	0.611
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.2-A		
	Plant	MODEL 1	MODEL 2
H2 Conversion, %	22.3	25.2	25.0
Ug, cm/sec		7.1	7.1
Gas hold-up, eps-g	0.265	0.178	0.178
kLa (uncorr), 1/s		0.531	0.531
kLa (corr), 1/s		0.324	0.324
kr.epsl, 1/s		0.025	0.025
KR(=kr.epsl.R.T/He)		0.004	0.004
KM(=kLa.R.T/He)		0.056	0.056
K(=KR.KM/(KR+KM))		0.004	0.004
H2+CO Conversion, %	21.1	26.6	26.4
CO Conversion, %	20.2	27.6	27.4
STY, nm ³ /h/m ³		106.5	105.7
STY, nm ³ /h/kg Fe		2.60	2.58
Mass Transfer Res., %		7.25	7.25
CO Conv., gmole/kg Fe/h	49.9	70.72	70.19
-CH2 produced, g/kg Fe/h		515.87	512.00
g/nm ³ syngas		52.80	52.40

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 30
COMPARISON WITH LAPORTE SBCR RUN AF-R6.2B

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	9.45	90.55	100
Density, g/cm ³	3.100	0.666	0.720
Volume % Solids	2.19	97.81	100.00
Viscosity, g/cm/s	-	0.0225	0.0266
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	95.7
Cat. Loading, kg/m ³	68.0

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	8.2
Feed Rate, am ³ /hr	76.0
nm ³ /hr	563.6
SV, am ³ /hr/m ³	54.0
nm ³ /hr/m ³	400.4
nm ³ /h/kg Fe	10.94
Corr. factor for kLa	0.613
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.2-B		
	Plant	MODEL 1	MODEL 2
H2 Conversion, %	19.4	22.9	22.7
Ug, cm/sec		7.2	7.2
Gas hold-up, eps-g	0.25	0.179	0.179
kLa (uncorr), 1/s		0.535	0.535
kLa (corr), 1/s		0.328	0.328
kr.epsl, 1/s		0.023	0.023
KR(=kr.epsl.R.T/He)		0.004	0.004
KM(=kLa.R.T/He)		0.056	0.056
K(=KR.KM/(KR+KM))		0.004	0.004
H2+CO Conversion, %	18.2	24.2	24.0
CO Conversion, %	17.3	25.1	24.9
STY, nm ³ /h/m ³		96.8	96.0
STY, nm ³ /h/kg Fe		2.65	2.62
Mass Transfer Res., %		6.46	6.45
CO Conv., gmole/kg Fe/h	46.9	71.98	71.41
-CH2 produced, g/kg Fe/h		525.01	520.89
g/nm ³ syngas		47.98	47.60

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 31
COMPARISON WITH LAPORTE SBCR RUN AF-R6.3A

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	8.44	91.56	100
Density, g/cm ³	3.100	0.666	0.714
Volume % Solids	1.94	98.06	100.00
Viscosity, g/cm/s	-	0.0225	0.0261
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	84.8
Cat. Loading, kg/m ³	60.2

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	2859
Inlet Gas Vel., cm/s	4.3
Feed Rate, am ³ /hr	39.4
nm ³ /hr	564.4
SV, am ³ /hr/m ³	28.0
nm ³ /hr/m ³	401.0
nm ³ /h/kg Fe	12.38
Corr. factor for kLa	0.615
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.3-A		
	Plant	MODEL 1	MODEL 2
H2 Conversion, %	32.0	27.7	26.9
Ug, cm/sec		3.6	3.7
Gas hold-up, eps-g	0.208	0.121	0.122
kLa (uncorr), 1/s		0.350	0.351
kLa (corr), 1/s		0.215	0.216
kr.eps1, 1/s		0.014	0.014
KR(=kr.eps1.R.T/He)		0.002	0.002
KM(=kLa.R.T/He)		0.037	0.037
K(=KR.KM/(KR+KM))		0.002	0.002
H2+CO Conversion, %	30.2	29.5	28.7
CO Conversion, %	28.8	30.7	29.9
STY, nm ³ /h/m ³		118.2	115.0
STY, nm ³ /h/kg Fe		3.65	3.55
Mass Transfer Res., %		6.28	6.27
CO Conv., gmole/kg Fe/h	88.4	99.81	97.05
CH2 produced, g/kg Fe/h		874.98	850.83
g/nm ³ syngas		70.70	68.75

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 32
COMPARISON WITH LAPORTE SBCR RUN AF-R6.3B

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	7.99	92.01	100
Density, g/cm ³	3.100	0.666	0.711
Volume % Solids	1.83	98.17	100.00
Viscosity, g/cm/s	-	0.0225	0.0259
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	79.9
Cat. Loading, kg/m ³	56.8

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	2859
Inlet Gas Vel., cm/s	4.3
Feed Rate, am ³ /hr	39.4
nm ³ /hr	564.4
SV, am ³ /hr/m ³	28.0
nm ³ /hr/m ³	401.5
nm ³ /h/kg Fe	13.14
Corr. factor for kLa	0.615
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.3-B		
	Plant	MODEL 1	MODEL 2
H2 Conversion, %	30.1	26.3	25.6
Ug, cm/sec		3.7	3.7
Gas hold-up, eps-g	0.221	0.122	0.122
kLa (uncorr), 1/s		0.351	0.352
kLa (corr), 1/s		0.216	0.217
kr.epsl, 1/s		0.014	0.014
KR(=kr.epsl.R.T/He)		0.002	0.002
KM(=kLa.R.T/He)		0.037	0.037
K(=KR.KM/(KR+KM))		0.002	0.002
H2+CO Conversion, %	27.8	28.0	27.3
CO Conversion, %	26.1	29.2	28.4
STY, nm ³ /h/m ³		112.4	109.5
STY, nm ³ /h/kg Fe		3.68	3.58
Mass Transfer Res., %		5.92	5.90
CO Conv., gmole/kg Fe/h	85.2	100.59	98.03
-CH2 produced, g/kg Fe/h		881.84	859.44
g/nm ³ syngas		67.13	65.42

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 33
COMPARISON WITH LAPORTE SBCR RUN AF-R6.4A

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	7.43	92.57	100
Density, g/cm ³	3.100	0.666	0.708
Volume % Solids	1.70	96.30	100.00
Viscosity, g/cm/s	-	0.0225	0.0256
Surface Tension, N/m	-	16.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.91
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.42
Catalyst Weight, kg	74.9
Cat. Loading, kg/m ³	52.6

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	4.0
Feed Rate, am ³ /hr	36.6
nm ³ /hr	271.3
SV, am ³ /hr/m ³	25.7
nm ³ /hr/m ³	190.5
nm ³ /h/kg Fe	6.73
Corr. factor for kLa	0.616
H2 Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.4-A		
	Plant	MODEL 1	MODEL 2
H2 Conversion, %	28.3	17.7	17.4
Ug, cm/sec		3.6	3.6
Gas hold-up, eps-g	0.157	0.120	0.120
kLa (uncorr), 1/s		0.346	0.346
kLa (corr), 1/s		0.213	0.213
kr,epsI, 1/s		0.008	0.008
KR(=kr,epsI.R.T/He)		0.001	0.001
KM(=kLa.R.T/He)		0.037	0.037
K(=KR.KM/(KR+KM))		0.001	0.001
H2+CO Conversion, %	28.8	19.4	19.0
CO Conversion, %	29.2	20.5	20.1
STY, nm ³ /h/m ³		36.9	36.2
STY, nm ³ /h/kg Fe		1.30	1.28
Mass Transfer Res., %		3.59	3.59
CO Conv., gmole/kg Fe/h	49.7	36.26	35.57
-CH2 produced, g/kg Fe/h		284.85	279.38
g/nm ³ syngas		42.30	41.49

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

TABLE 34
COMPARISON WITH LAPORTE SBCR RUN AF-R6.4B

PROPERTIES OF SOLID AND LIQUID			
	Solid	Liquid	Slurry
Wt% Solids in Slurry	7.17	92.83	100
Density, g/cm ³	3.100	0.666	0.706
Volume % Solids	1.63	98.37	100.00
Viscosity, g/cm/s	-	0.0225	0.0255
Surface Tension, N/m	-	18.5	-
Part. Size, microns	10.0	-	-

BUBBLE COLUMN DIMENSIONS	
	LaPorte
ID of Rx, cm	57.2
L of Rx, cm	609.6
Slurry Level, fraction	0.90
Rx X-section, m ²	0.26
Slurry Volume, m ³	1.41
Catalyst Weight, kg	71.2
Cat. Loading, kg/m ³	50.6

OPERATING CONDITIONS	
Rx Temperature, K	538
Rx Pressure, kPa	1480
Inlet Gas Vel., cm/s	4.0
Feed Rate, am ³ /hr	36.6
nm ³ /hr	271.3
SV, am ³ /hr/m ³	26.0
nm ³ /hr/m ³	192.8
nm ³ /h/kg Fe	7.08
Corr. factor for kLa	0.616
H ₂ Diffusivity, cm ² /s	0.00057

BUBBLE COLUMN MODEL CALCULATIONS			
RUN	AF-R6.4-B		
	Plant	MODEL 1	MODEL 2
H ₂ Conversion, %	28.3	16.6	16.6
U _g , cm/sec		3.6	3.6
Gas hold-up, eps-g	0.157	0.121	0.121
kLa (uncorr), 1/s		0.347	0.347
kLa (corr), 1/s		0.214	0.214
kr.epsl, 1/s		0.008	0.008
KR(=kr.epsl.R.T/He)		0.001	0.001
KM(=kLa.R.T/He)		0.037	0.037
K(=KR.KM/(KR+KM))		0.001	0.001
H ₂ +CO Conversion, %	28.8	18.4	18.1
CO Conversion, %	29.2	19.5	19.2
STY, nm ³ /h/m ³		35.4	35.0
STY, nm ³ /h/kg Fe		1.30	1.28
Mass Transfer Res., %		3.45	3.45
CO Conv., gmole/kg Fe/h	49.8	36.18	35.73
-CH ₂ produced, g/kg Fe/h		284.21	280.69
g/nm ³ syngas		40.15	39.66

Model 1: Both gas and liquid in plug flow

Model 2: Gas in plug flow and liquid completely mixed

FIGURE A-1
SUMMARY DATA FOR RUHRCHEMIE CATALYST - RUN 31

FIGURE A-2
SUMMARY DATA FOR RUHRCHEMIE CATALYST - RUN 31

FIGURE A-3
SUMMARY DATA FOR RUHRCHEMIE CATALYST - RUN 31

FIGURE A-4
SUMMARY DATA FOR RUHRCHEMIE CATALYST - RUN 31

FIGURE A-5
SUMMARY DATA FOR RUHRCHEMIE CATALYST - RUN 31

FIGURE A-6
SUMMARY DATA FOR RUHRCHEMIE CATALYST - RUN 31

FIGURE A-7
SUMMARY DATA FOR RUHRCHEMIE CATALYST - RUN 31

FIGURE A-8
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 44

TEMP., °C	280	265
FEED, NL/H g Fe	2.0	2.4
PRESSURE, PSIG	153	290
FEED LOT #	<div style="display: flex; justify-content: space-around; align-items: center;"> ← A → ↔ B ↔ </div>	

**CO
CONVERSION**

FIGURE A-9
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 44

FIGURE A-10
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 44

FIGURE A-11
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 44

FIGURE A-12
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 44

FIGURE A-13
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 44

FIGURE A-14
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 44

FIGURE A-15
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 48

FIGURE A-16
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 48

FIGURE A-17
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 48

FIGURE A-18
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 48

FIGURE A-19
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 48

FIGURE A-20
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 48

FIGURE A-21
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 48

FIGURE A-22
SUMMARY DATA FOR UCI-"O" CATALYST - RUN 48

FIGURE A-23
SUMMARY DATA FOR UCI-"A" CATALYST - RUN 50

FIGURE A-24
SUMMARY DATA FOR UCI-"A" CATALYST - RUN 50

FIGURE A-25
SUMMARY DATA FOR UCI-"A" CATALYST - RUN 50

FIGURE A-26
SUMMARY DATA FOR UCI-"A" CATALYST - RUN 50

FIGURE A-27
SUMMARY DATA FOR UCI-"A" CATALYST - RUN 50

FIGURE A-28
SUMMARY DATA FOR UCI-"A" CATALYST - RUN 50

FIGURE A-29
SUMMARY DATA FOR UCI-"A" CATALYST - RUN 50

FIGURE A-30
SUMMARY DATA FOR UCI-"B" CATALYST - RUN 51

FIGURE A-31
SUMMARY DATA FOR UCI-"B" CATALYST - RUN 51

FIGURE A-32
SUMMARY DATA FOR UCI-"B" CATALYST - RUN 51

FIGURE A-33
SUMMARY DATA FOR UCI-"B" CATALYST - RUN 51

FIGURE A-34
SUMMARY DATA FOR UCI-"B" CATALYST - RUN 51

FIGURE A-35
SUMMARY DATA FOR UCI-"B" CATALYST - RUN 51

FIGURE A-36
SUMMARY DATA FOR UCI-"START-UP" CATALYST - RUN 53

FIGURE A-37
SUMMARY DATA FOR UCI-"START-UP" CATALYST - RUN 53

FIGURE A-38
SUMMARY DATA FOR UCI-"START-UP" CATALYST - RUN 53

FIGURE A-39
SUMMARY DATA FOR UCI-"START-UP" CATALYST - RUN 53

FIGURE A-40
SUMMARY DATA FOR UCI-"START-UP" CATALYST - RUN 53

FIGURE A-41
SUMMARY DATA FOR UCI-"START-UP" CATALYST - RUN 53

FIGURE A-42
SUMMARY DATA FOR UCI-"COMPOSITE" CATALYST - RUN 54

FIGURE A-43
SUMMARY DATA FOR UCI-"COMPOSITE" CATALYST - RUN 54

FIGURE A-45
SUMMARY DATA FOR UCI-"COMPOSITE" CATALYST - RUN 54

FIGURE A-46
SUMMARY DATA FOR UCI-"COMPOSITE" CATALYST - RUN 54

FIGURE A-47
SUMMARY DATA FOR UCI-"COMPOSITE" CATALYST - RUN 54

FIGURE A-48
SUMMARY DATA FOR UCI-"COMPOSITE" CATALYST - RUN 54

TABLE B-1
WEIGHT OF PRODUCTS COLLECTED IN TRAPS FOR RUN 44

(All weights are in grams)

Time-on-Stream, hours	Hot Trap	Ice Trap		Cryogenic Trap
		Hydrocarbon	Aqueous	
12	35	4	11	9
24	10	7	5	5
48	23	18	14	7
72	179	28	15	24
96	147	28	16	19
120	148	28	19	34
144	172	20	17	17
168	159	27	14	20
192	168	26	16	20
216	189	30	18	33
240	131	24	18	17
264	114	35	16	3
288	130	28	14	22
312	164	32	14	22
336	93	18	28	17
360	95	16	33	18
384	163	29	7	13
408	128	37	15	32
432	90	35	13	27
456	169	34	15	24
480	97	34	13	10
504	150	37	13	17
TOTAL	2754	575	326	410

TABLE B-2
WEIGHT OF PRODUCTS COLLECTED IN TRAPS FOR RUN 48

(All weights are in grams)

Time-on-Stream, hours	Hot Trap		Ice Trap		Cryogenic Trap
	Wax	Condensate	Hydrocarbon	Aqueous	
12	trace	18	17	16	-
24	1	10	18	5	17
48	5	3	41	17	11
72	trace	19	50	15	11
96	-	-	45	16	14
120	7	22	57	14	3
144	98	-	49	15	20
163	81	41	53	12	17
TOTAL	192	113	330	110	93

TABLE B-3
WEIGHT OF PRODUCTS COLLECTED IN TRAPS FOR RUN 50

(All weights are in grams)

Time-on-Stream, hours	Hot Trap		Ice Trap		Cryogenic Trap	
	Wax	Condensate	Hydrocarbon	Aqueous	1	2
12	1	20	22	12	15	6
24	1	8	15	10	1	3
48	4	34	55	21	14	4
72	52	67	58	17	13	24
96	30	125	55	19	15	10
120	189	55	38	19	11	9
144	177	36	34	23	9	5
168	148	23	41	19	13	8
192	128	26	41	19	11	10
216	128	20	41	19	11	6
240	138	26	39	19	12	6
264	47	19	39	11	8	4
276	64	14	19	10	7	3
TOTAL	1107	473	497	218	140	98

TABLE B-4
WEIGHT OF PRODUCTS COLLECTED IN TRAPS FOR RUN 51

(All weights are in grams)

Time-on-Stream, hours	Hot Trap		Ice Trap		Cryogenic Trap	
	Wax	Condensate	Hydrocarbon	Aqueous	1	2
12	4	13	22	13	5	-
24	3	13	26	17	2	2
48	5	24	43	45	7	2
72	340	34	41	60	10	7
96	6	27	48	65	9	5
120	6	29	48	61	10	4
144	8	27	54	62	10	5
168	181	33	55	63	16	9
192	8	32	59	60	7	6
216	68	34	52	56	12	10
240	8	36	62	56	15	9
264	52	37	60	54	10	6
288	55	35	60	49	16	15
312	57	38	58	48	19	13
336	142	135	56	45	22	6
360	30	42	64	46	22	13
TOTAL	532	499	808	800	192	112

TABLE B-5
WEIGHT OF PRODUCTS COLLECTED IN TRAPS FOR RUN 53

(All weights are in grams)

Time-on-Stream, hours	Hot Trap		Ice Trap		Cryogenic Trap	
	Wax	Condensate	Hydrocarbon	Aqueous	1	2
12	2	4	21	3	2	tr
24	2	9	25	8	9	15
48	2	23	51	22	19	8
72	2	30	48	23	13	7
96	27	172	33	28	8	5
120	24	115	25	33	13	3
144	28	113	37	20	15	12
168	36	62	39	25	11	7
192	122	22	53	34	98	11
216	111	128	58	38	13	10
240	135	56	47	32	10	9
264	87	32	27	8	6	0
288	119	19	21	9	7	6
312	103	28	19	12	8	5
336	137	8	25	13	13	5
360	137	18	26	11	11	7
384	125	5	29	12	13	5
TOTAL	1199	844	584	331	269	115

TABLE B-6
WEIGHT OF PRODUCTS COLLECTED IN TRAPS FOR RUN 54

(All weights are in grams)

Time-on-Stream, hours	Hot Trap		Ice Trap		Cryogenic Trap	
	Wax	Condensate	Hydrocarbon	Aqueous	1	2
12	3	22	6	8	2	2
24	-	28	15	7	5	8
48	6	29	31	5	17	7
72	50	24	30	19	12	5
96	66	29	19	23	16	3
120	169	26	19	25	22	6
144	91	47	25	20	17	4
168	149	37	23	19	12	67
192	122	36	25	18	12	7
216	94	109	30	27	10	5
240	20	152	44	28	9	7
264	80	101	44	39	5	5
288	221	41	50	63	23	9
312	203	37	57	53	18	6
336	-	-	58	49	17	10
360	147	31	57	44	25	8
384	160	22	44	31	16	6
408	10	15	32	14	12	2
432	38	10	29	13	10	3
456	131	17	23	12	12	4
490	39	10	26	11	7	5
504	84	8	42	6	-	-
TOTAL	1883	831	729	534	279	179