Solar Photo-Thermal Catalytic Reactions to Produce High Value Chemicals

H.W. Prengle, Jr. and W.E. Wentworth
University of Houston
Houston, Texas

NREL Technical Monitor: R. Gerald Nix

National Renewable Energy Laboratory
(formerly the Solar Energy Research Institute)
1617 Cole Boulevard
Golden, Colorado 80401-3393
A Division of Midwest Research Institute
Operated for the U.S. Department of Energy
under Contract No. DE-AC02-83CH10093

MASTER

Prepared under Subcontract No. XX-7-07028-1

April 1992

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This report describes subcontracted research. The report is unreviewed and expresses only the opinions of the author[s]. It has been prepared for reproduction from the best available copy.

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Microfiche A01
Printed Copy A03

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issue of the following publications which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

Topical Report

SOLAR PHOTO-THERMAL CATALYTIC REACTIONS TO PRODUCE HIGH VALUE CHEMICALS

By
H. William Prengle, Jr. and Wayne E. Wentworth
Principal Investigators
Chemical Engineering and Chemistry Departments and The Energy Laboratory
University of Houston, Houston, Texas 77004

SERI Contract XX-7-07028-1

SUMMARY

This report presents a summary of the research work accomplished to date on the utilization of solar photo-thermal energy to convert low cost chemical feedstocks into high \$-value chemical products. The rationale is that the solar IR-VIS-UV spectrum is unique, supplying endothermic reaction energy as well as VIS-UV for photochemical activation. Chemical market analysis and product price distribution focused attention on speciality chemicals with prices >\$1.00/lb, and a synthesis sequence of n-paraffins to aromatics to partial oxidized products.

The experimental work has demonstrated that enhanced reaction effects result from VIS-UV irradiation of catalytically active V_2O_5/SiO_2 . Experiments of the past year have been on dehydrogenation and dehydrocyclization of n-paraffins to olefins and aromatics with preference for the latter. Recent results using n-hexane produced 95% conversion with 56% benzene; it is speculated that aromatic yield should reach ~70% by further optimization.

Pilot- and commercial-scale reactor configurations have been examined; the odds-on-favorite being a shallow fluid-bed of catalyst with incident radiation from the top. Sequencing for maximum cost effectiveness would be day-time endothermic followed by night-time exothermic reactions to produce the products.

31 March 1988

. TABLE OF CONTENTS .

Introduction	page 2
Objectives of the Research	2
Candidate Chemical Reactions & Products	3
Figure 1- Sales Price Histogram of Chemicals	4
Table 1- Favorable Synthesis Reactions	5
Table 2- Synthesis Products: Sales Price-Cost Ratio	6
Figure 2- Energy Source & Utilization	8
Objectives of the Experimental Work	8
Experimental Progress to date	10
Results for Hydrocarbon Reforming Reactions	12
Figure 3- Product Profiles for Reforming Hexane	14
Table 3- Effect of V ₂ O ₅ (13% Al ₂ O ₃) Ratio	14
Table 4- Effect of Catalyst Support on Hexane Reforming	16
Table 5- Effect of V ₂ O ₅ /SiO ₂ Ratio on ...	17
Table 6- Effect of Radiant Power with Helium Carrier Gas	17
Table 7- Effect of Radiant Power with Argon Carrier Gas	18
1988 Experimental Work	19
Expected Outcome of 1988 Experimental Work	19
Present View - Process Paths & Configurations	20
Figure 4- Reaction & Process Pathways	21
Preliminary Economics - Price Advantage Ratios	22
Table 8- Price Advantage Ratio, PAA Path	23
Table 9- Comparative Ra and Va Values	23
Comparative Commercial Processes	23
Preliminary Conclusions	24
Selected References	26
APPENDIX	
Light Source	27
Selection of Potential Photo-Catalysis	27

INTRODUCTION

Solar energy with its broad spectral distribution of infra red, visible and ultra violet (IR-VIS-UV) radiation can be used not only for thermal power generation, but also for chemical manufacture. For the latter the unique properties of the sun's spectrum permits the VIS-UV to be used for catalytic reaction activation, while the IR can supply needed endothermic energy to produce lower cost higher energy products.

The work described in this report is being conducted by a multidisciplinary research group in the Chemistry, Physics, and Chemical Engineering Departments of the University of Houston. In order to produce a basis for understanding the phenomena involved, leading to the development of process technology, the research is being carried out under the subprojects of: 1) photo-thermal chemical reactions, 2) mechanisms of photo-enhancement, and 3) candidate reaction selection, engineering analysis and process development.

The overall objective of the project is to develop a new catalytic, more highly selective, reaction technology utilizing the sun's radiation, leading to a process for the production of high \$-value organic chemical product(s), from readily available low cost petroleum-petrochemical feed stocks. And which will show substantial economic advantage as lower unit product cost over conventional methods of manufacture.

The experimental work to date has clearly demonstrated that enhanced reaction effects, i.e. higher reaction rates and yields (selectivity) at lower temperatures, result from VIS-UV irradiation of certain catalytically active transition metal oxides. These effects could well represent an extension of work being carried out and presented in the literature by chemists, on catalytic active site transitions which enhance reaction, and a break-through in chemical process chemistry.

OBJECTIVES OF THE RESEARCH

The following specific objectives focus attention on the experimental and analytical research currently being conducted.

1) Photo-Catalytic Dehydrocyclization of Paraffins to Aromatics- chemical transformation of n-paraffins to aromatics, for example, is a recognized important commercial process [1,2]. The objective is to accomplish this reaction photo-catalytically at less severe conditions with greater yield, and at lower cost.

2) Photo-Catalytic Alkylation-Hydroxylation of Aromatics- will result in a significant multiplier on product sales price, The objective is to produce an oxygenated aromatic product, for example a cresol (intermediate for resins and

esters), in a one-step photo-catalytic process.

3) Photo-Catalysts of High Activity and Selectivity- literature data indicates that activation of transition metal oxide (semi-conductors) catalysts (e.g. vanadium pentoxide, V_2O_5) primarily occurs in the visible [3,6,14] for highly loaded catalysts, UV being much less important, a plus since the earth's surface solar spectrum has a relatively minor amount of UV. The objective is to determine the optimum combination of mixed oxides and loading, and support structure ($SiO_2-Al_2O_3$), for maximum conversion (selectivity) to the desired product.

4) Photo-Catalytic Reactor Configuration- for optimum results one must satisfy the conditions of, complete irradiation of all catalyst particles by high energy dispersion and rapid bed turnover, and efficient gas-solid contacting; a shallow fluid bed of microspheroidal catalyst particles is the odds-on best choice. The objective is to carry out the experimental runs in a similar configuration.

5) Process Configuration- recognizing that in the ultimate engineering configuration the process will have to be totally integrated between day and night operation to be cost effective, a sequential combination of reactions are required. The objective is to determine other compatible exothermic reactions, with the same catalyst and reactor configuration, which will extend the synthesis path to additional high \$-value products.

CANDIDATE CHEMICAL REACTIONS & PRODUCTS

In order to guide the selection of possible reactions a set of four (4) criteria were established: 1) -the reaction must be endothermic and thermodynamically favorable; 2) - the reaction must be conventionally catalytic; 3) -the product must be synthesized from low cost feedstocks; and 4) -the product must be of high \$-value (sales price \$1.00 /lb). A detailed investigation was conducted resulting in two primary outcomes:

Firstly, a sales price histogram of some 250 chemical products [4], presented as Figure 1, indicated a bimodal distribution leading to the following four-group classification:

a) Primary Feedstocks	0 - 0.33	\$/lb
b) Intermediates	0.20 - 0.50	
c) Commodity Products	0.50 - 1.00	
d) Speciality Chemicals	> 1.00	

Clearly, while the classification of the latter three groups overlap somewhat, we are primarily seeking synthesis of the latter group, specialty chemicals, from primary feedstocks.

Secondly, thermodynamic calculations on possible endothermic synthesis

**Figure 1. SALES PRICE HISTOGRAM OF
CHEMICAL PRODUCTS**

reactions indicated that a number of cyclization and cyclization-addition (alkylation and hydroxylation) reactions are favorable, and also lead to high \$-value products. A list of fifteen (15) pertinent reactions is presented as Table 1[4]; the latter ten satisfy the aforementioned criteria. In addition, Table 2 [4] gives the sales price - reactant cost ratio.

Reactionwise our present thinking is moving along two paths: the first, direct endothermic synthesis of aromatics by dehydrocyclization (dehydrogenation + cyclization) of n-paraffins, followed by hydroxylation with methanol to give the final cresol product. And the second, exothermic oxidation of aromatics with air to high \$-value aldehydes and acids. The latter could satisfy the aforementioned day-night combination. As an illustration, first consider the synthesis of cresol from n-heptane + methanol, toluene is formed and then hydroxylated,

TABLE 1.
. FAVORABLE SYNTHESIS REACTIONS .

Reaction	Products	$\Delta H_R^\circ(298)$	$\Delta H_R^\circ(500)$	Product Value (\$/lb)
1) $n\text{-C}_6\text{H}_{14}$	benzene	59.78	62.02	0.123
2) $n\text{-C}_6\text{H}_{14} + \text{CH}_3\text{OH}$	toluene	42.17	44.95	0.190
3) $n\text{-C}_6\text{H}_{14} + \text{CH}_3\text{OH}$	phenol	47.12	49.98	0.290
4) $n\text{-C}_6\text{H}_{14} + \text{NH}_3$	aniline	71.65	74.90	0.420
5) $n\text{-C}_6\text{H}_{14} + 2\text{CH}_3\text{OH}$	Resorcinol	31.24	36.35	p 1.950 m 1.790 o 1.686
6) $\text{C}_6\text{H}_5\text{CH}_3 + \text{H}_2\text{O}$	o-cresol	15.88	16.67	p 1.150 m 1.650 o 0.870
7) $n\text{C}_6\text{H}_{14} + \text{CH}_3\text{OH}$	m-cresol	56.41	59.97	"
8) $\text{C}_6\text{H}_5\text{OH} + \text{CO}_2$	salicylic acid	17.58	16.04	1.680
9) $\text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_3\text{CHO}$	CH_3CONH - acetanilide	2.72	4.30	1.29
10) $\text{C}_6\text{H}_5\text{CH}_3 + \text{H}_2\text{O}$	benzaldehyde	27.85	29.08	1.25
11) $\text{C}_6\text{H}_6 + \text{CH}_3\text{OH}$	benzyl alcohol	4.27	6.87	1.32
12) $\text{C}_6\text{H}_5\text{CH}_3 + \text{NH}_3$	2,4-xylidine	19.37	21.18	1.50
13) $\text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{OH}$	guaiacol	11.91	11.78	2.70
14) $\text{CH}_2=\text{CHCH}_3 + \text{HBr}$	$\text{CH}_2=\text{CHCH}_2\text{Br}$ ally bromide	15.58	16.29	5.50
15) $n\text{-C}_8\text{H}_{18} + \text{NH}_3$	ethylaniline	74.14	76.51	1.58

TABLE 2.
. PRODUCT PRICE / REACTANT COST RATIO .

REACTION	REACTANT COST(\$/lb)		PRODUCT	PRODUCT VALUE(\$/lb)	RATIO = Product Price Reactant(s) Cost
1a) nC_6H_{14}	0.089		benzene	0.123	1.54
* 1b) nC_8H_{18}	0.089		ethylbenzene	0.230	2.58
2) $nC_6H_{14} + CH_3OH$	0.168		toluene	0.190	1.13
3) $nC_6H_{14} + CH_3OH$	0.168		phenol	0.290	1.73
4) $nC_6H_{14} + NH_3$	0.174		aniline	0.420	2.41
5) $nC_6H_{14} + 2CH_3OH$	0.247		resorcinol	1.95 (p) 1.79 (m) 1.69 (o)	7.89 7.25 6.83
6) $C_6H_5CH_3 + H_2O$	0.195		o-cresol	1.15 (p) 1.65 (m) 0.87 (o)	5.90 8.46 4.46
7) $nC_6H_{14} + CH_3OH$	0.168		m-cresol	1.15 (p) 1.65 (m) 0.87 (o)	6.85 9.82 5.18
8) $C_6H_5OH + CO_2$	0.340		salicylic acid	1.68	4.94
9) $C_6H_5NH_2 + CH_3CHO$	0.790		acetanilide	1.29	1.63
10) $C_6H_5CH_3 + H_2O$	0.195		benzaldehyde	1.25	6.41
11) $C_6H_6 + CH_3OH$	0.202		benzyl alcohol	1.32	6.53
12) $C_6H_5CH_3 + NH_3$	0.275		2,4-xylidine	1.50	5.45
13) $C_6H_5OH + CH_3OH$	0.369		guaiacol	2.70	7.32
14) $CH_2=CHCH_3 + HBr$	0.545	$CH_2=CHCH_2Br$	allyl bromide	5.50	10.1
15) $nC_8H_{18} + NH_3$	0.174		ethylaniline	1.58	9.08

* added to table

and even the ground-state thermodynamics are favorable at $T > 500\text{K}$,

$$\Delta H_{R^0}(500\text{K}) = 47.82 \text{ kcal/mole}; \quad \Delta F_{R^0} = -2.141; \quad \ln K_a = 2.155$$

For the second reaction path, i.e. air oxidation, toluene to benzaldehyde is chosen as the example,

the product has high \$-value (Tables 1 & 2), and the thermodynamic values are highly favorable,

$$\Delta H_{R^0}(500\text{K}) = -56.60 \text{ kcal/mole}; \quad \Delta F_{R^0} = -78.55; \quad \ln K_a = 79.1$$

For the first reaction path it is appropriate at this point to discuss our theory of the spectral energy utilization and two important related questions: How much energy is required, and where does the energy come from? Using reaction (1) above as the example, and the thermodynamic values, it follows that for the reactants there is a net of 2, C-C bonds and 8, C-H bonds broken, and for the products a net of 3, C=C bonds and 4, H-H bonds formed, for an overall endothermic requirement of $\Delta H_{R^0} = 47.8 \text{ kcal/mole}$. An additional amount of energy, over and above the 47.8 kcal/mole, is required to maintain a population of activated catalyst sites for activated reaction. How much this will be is not known at present; the experimental work should reveal the answer. We very roughly estimate that 1/4 to 1/3 of the endothermic energy will be required. From the solar spectrum there are two sources of energy, VIS-UV and IR. The VIS-UV is absorbed by the catalyst active sites, causing the transition $\text{V}=\text{O} \longrightarrow \text{V}=\text{O}^*$, continuous irradiation producing a relatively large population of the activated sites, $\text{V}=\text{O}^*$. The IR is absorbed by the catalyst particles, acting as a secondary heat source, to supply the endothermic reaction energy. The entire process of energy transfer and utilization is illustrated by Figure 2.

Figure 2. ENERGY SOURCE & UTILIZATION

OBJECTIVES OF EXPERIMENTAL WORK

OVERALL OBJECTIVE - The objective of our experimental work is to demonstrate the feasibility of using high flux radiant energy (ie. concentrated solar radiation) to initiate and sustain endothermic chemical reactions. An effort will be made to show that this form of energy input is a viable alternative to conventional thermal energy input. In some cases it may even offer distinct advantages. These will be investigated and exploited as they are identified. Emphasis will be placed on reactions which are commercially important.

RATIONALE - High flux radiant energy, such as solar radiation, differs from thermal energy obtained from fossil fuels in at least three significant ways. First, radiant energy can be optically concentrated and focussed so that it can be transferred directly into a reaction medium without the use of heat exchangers. Second, radiant energy has the potential for producing very high local (eg. catalyst surface) temperatures. Reactants can be decomposed under unusual, non-equilibrium conditions. This may lead to products not normally produced under more conventional thermal

conditions. Third, radiant energy has the potential to interact directly with a catalyst or with a catalyst/reactant complex by a photochemical (eg. excited electronic state) mechanism. This can, in principle, lead to reactions not possible with purely thermal energy input. Only a small portion of the solar spectrum is sufficiently energetic to interact by a direct photochemical process with most catalysts or catalyst/reactant complexes. Most of the radiation will, of course, be degraded to thermal energy upon absorption. However, if a photochemical process occurs and if this process produces an excited molecule or free radical which initiates an endothermic chemical reaction, then the thermal energy will also be consumed. This can result in a very efficient utilization of the radiant energy. Both effects, non-equilibrium heating and photochemical, will be tested for and distinguished when possible.

METHOD - In this research, the solar spectrum is simulated by the emission from a high pressure xenon lamp. Radiation from this lamp is directed into a reactor to the reaction medium through a quartz window. In order to use the radiant energy as proposed, an absorbing species must be part of the reaction medium. Most chemical reactants will not absorb the entire solar spectrum. Some will absorb only a small portion: many none at all. In order to overcome this problem, we have elected to use a darkened, catalyst coated surface to absorb the radiant energy. Many potential catalysts (eg. metal oxides) are themselves colored and form a naturally dark surface when deposited on an appropriate support. Two methods for providing reactant-catalyst contact in the presence of high flux radiant energy have been selected for investigation. In the first method, small (50-80 microns diameter) particles of an appropriate support (eg. silica, alumina, etc.) are coated with catalyst. These particles comprise a fluid bed which is supported inside a reactor by a porous frit. An inert carrier gas is passed upward through the frit to fluidize the bed. Only the top surface of the bed is illuminated. In the second method, catalyst is coated directly onto a porous frit made of an appropriate material and the top surface of the frit is illuminated inside the reactor. In either case, reactant is entrained in the carrier gas and is adsorbed onto the catalyst coated surfaces as the gas passes through the illuminated frit or bed. Reaction products are swept away by the carrier gas and are measured downstream by a gas chromatographic analytical system. For a given reactant, product yields are measured as a function of catalyst type, catalyst/support ratio, and light intensity. Results are compared to those for the same reactions when run with conventional thermal energy input. Reactions for which the radiant energy input results are significantly different from the thermal energy are studied further. For these reactions, product yields are measured with various optical cut off filters inserted in the light beam to remove selected portions of the emission spectrum. In these experiments the total optical flux is held constant as the filters are changed. A dependence of product yield on wavelength is interpreted as indicating a true photochemical effect.

EXPERIMENTAL PROGRESS TO DATE

LIGHT SOURCE - In this research, the emission from a high pressure xenon arc lamp is used to provide the radiant input energy to a reactor. Two lamp systems have been purchased, installed, and characterized. Details of this work are given in the Appendix of this report.

REACTOR DESIGN - In our early experiments, we used reactors consisting of simple quartz tubes with side-arms and an o-ring sealed quartz window at the top. A quartz frit was permanently built into the reaction tube and the catalyst/support systems were mostly of the fluid bed particle type. With this type of reactor, it was difficult to control the reaction temperature even to a nominal value, since there was no provision for controlled heat removal. It was also difficult to use catalyst coated frits in these reactors. We now use specially constructed stainless steel reactors which contain removable frits so that both particle bed and frit supported catalysts can be used conveniently. The internal shape of the reaction chamber is conical. A quartz window is o-ring sealed to the large (top) end of the cone, and a frit is compression sealed to the small (bottom) end. Carrier gas enters the reaction zone through the frit. The walls of the cone can be water cooled as required.

Reactants are added to the carrier gas before the frit either by pulsed injection or by continuous injection. In the continuous injection mode, a high precision pump is used to inject liquids (typically 1-10 $\mu\text{l}/\text{min}$) and a pressurized tank and flow-regulating valve are used to inject gases at constant rate. This mode provides data from which reaction rates can easily be calculated, but can only be used with catalysts which are not rapidly deactivated. In the pulsed injection mode, a 10 port switching valve is used. Two sample loops (typically 1.5 μl internal volume for liquids and 15 μl internal volume for gases) are attached to this valve so that either one or two reactants can be added in a single pulse or plug. Using a carrier gas flow rate of 15 cm^3/min , the entire reactant pulse can be injected in 0.06 sec. The loops are loaded manually with a syringe, but the valve is switched automatically so that the time between reactant injection and product sampling can be measured precisely by our analytical data system. By varying the time delay between reactant injection and product sampling we can measure the time profile of product concentrations as they are released from the catalyst surface. These distributions can be used to obtain some information about reaction mechanism. This method is also most useful with catalysts which are rapidly deactivated, since reactant is in contact with the catalyst for only a small fraction of the total run time which includes a rather long product separation step.

Reaction products are entrained in the carrier gas and transported from the reactor to another 10 port switching valve which is also controlled by our analytical data system. This valve is used to remove

a sample (typically 6 μ l) of the reactor effluent for analysis.

Different carrier gases can be used. We have typically used either helium or argon. In some cases the nature of the carrier gas, although nominally inert, was found to have a significant effect on the results obtained.

ANALYTICAL SYSTEM - We have developed a special multi-column gas chromatographic system for analyzing the reactor gas effluent. The polar components in the sample are separated from the non-polar components on a pre-column. Each of the two fractions are then further separated on separate columns. This requires use of three separate column ovens and a third switching valve. The sequencing of all of the switching valves is controlled by the microprocessor associated with an 8300 Series Perkin Elmer gas chromatograph. The polar and non-polar eluents are measured by a single FID detector. The microprocessor is also used to measure the peak area associated with each of the product compounds detected.

REACTION SCREENING PROCEEDURE - The first step in our screening procedure is to compare the reaction products and relative yields we obtain with radiant energy input for a given reactant/catalyst/support system to those reported in the literature as obtained with heat input. For this initial screening of catalyst, support, and reaction parameters, we have measured the percent yield and amount of product produced based on the theoretical relative response of the flame ionization detector (FID) to each product rather than on calibrated response factors. As a first approximation, the FID response to a given compound is directly proportional to the number of carbon atoms in the compound. Since the masses of the hydrocarbon products of interest are dependent primarily on their carbon content, the relative FID responses to these compounds represent the approximate weight percentages of the products measured.

Reactant/catalyst/support systems which give different products or which give the same products but in significantly different relative yields are investigated further in an attempt to determine if the difference is due to a photocatalytic effect or simply to a difference in the way the catalyst/support is heated. In our early experiments, we attempted to screen reaction/catalyst/support systems for a photocatalytic effect by comparing reaction rates obtained with heat input from an external furnace to reaction rates measured with radiant energy input from our lamp systems. Although these experiments showed some indication that radiant energy gave rates which were different, the results were not conclusive. Two problems were identified. First, heat input by conduction produces a temperature gradient in the catalyst/support which is quite different from that produced when the catalyst/support is irradiated on its upper surface only. This makes it difficult to define reaction

temperature precisely and to obtain thermal and photo data under comparable conditions. Second, with radiant energy input, both thermal and photocatalyzed reactions can occur simultaneously. This makes it difficult to distinguish the presence of a photo effect when reaction rate data are all that can be measured experimentally. We now use a screening procedure which is based on the use of optical cut-off filters which selectively remove portions of the spectrum from the light beam used to irradiate the catalyst surface. We have carefully measured the optical filtering characteristics of each of our filters using uv-visible and infra-red spectroscopy, and have measured the percentage of energy each removes from the incident light beam by calorimetry. Filters are inserted into the light beam one at a time. Each time a filter is inserted, the lamp output is adjusted so that the total energy reaching the catalyst surface is constant although it is comprised of a different spectral distribution. A dependence of product yield on spectral distribution is interpreted as indicative of a photocatalytic effect.

When the cut-off filters are used with our 150 W system, no other attenuation of the lamp emission is necessary. When the cut-off filters are used with our 1000 W system, we must also use an IR (water) filter. The total output energy of the larger lamp, even when operated at only moderate levels, is so great that it fractures the glass cut-off filters. The water filter removes a portion of the long wavelength end of the lamp emission, thus reducing the total energy in the light beam without removing the uv-visible wavelengths most likely to produce photocatalysis.

SELECTION OF POTENTIAL PHOTOCATALYSTS - A survey of the available chemical literature has convinced us that vanadium pentoxide (V_2O_5) is a catalyst which is very likely to provide the photocatalytic activity desired. Details are given in the Appendix of this report.

CATALYST PREPARATION - Various methods for preparing V_2O_5 catalysts have been tested. In the method selected, the support material is impregnated with ammonium vanadate or with vanadyl acetylacetonate. This is done by soaking the support (particles or frits) in a solution of the vanadium salt and then slowly evaporating the solvent, leaving the salt evenly distributed throughout the porous support. After evaporation of the solvent, the catalyst/support is calcined at 520 °C for 3 hours in an oxygen atmosphere. This converts the salt to V_2O_5 irrespective of the composition and oxidation state of the vanadium salt used for impregnation. Samples of each V_2O_5 /support system were prepared with different V_2O_5 loadings ranging from 0.25 to 10 weight percent V_2O_5 .

RESULTS FOR HYDROCARBON REFORMING REACTIONS

Hydrocarbon reforming reactions are of commercial importance, are presently run using thermal energy input, and are known to be catalyzed by V_2O_5/SiO_2 [Lee, Fu M. U. S. Patent 4 607 129,

1986]. Preliminary studies indicated that under appropriate conditions we could form benzene from n-hexane and substituted benzene from higher molecular weight normal aliphatic hydrocarbons using radiant energy input. We have further studied the reaction of hexane using high flux radiant energy from our 1000 W system and V_2O_5 on four supports: 13% Al_2O_3/SiO_2 particles (60 microns dia.), 25% Al_2O_3/SiO_2 particles (65 microns dia.), 100% SiO_2 particles (63-88 microns dia.), and a porous quartz frit. Use of the porous frit supported catalyst produced cracking of these reactants, while use of the particle supported catalysts produced reforming of these reactants. Each of the V_2O_5 /particle catalysts was used in a metal reactor as a shallow (~2-3 mm deep) bed supported on a stainless steel frit.

Liquid hydrocarbon reactant was added to the carrier gas entering the reactor using the pulsed injection (1.5 μ l/pulse) method (see above). Since we observed that the catalysts gradually become deactivated due to carbon formation, time profiles were measured only for selected reactions. Collection of the 8-10 data points required for a profile of a single product requires about 10 hours and it is important to maintain a constant catalytic activity throughout the data collection period. This can be done either by limiting the number of reactant samples to which a particular catalyst sample is exposed, as was done in our early experiments, or by regenerating the catalyst between reactant pulses, as was done in most of our more recent work. In principle, carbon formation can be retarded by adding H_2 or H_2O (steam) to the carrier gas. We have tried using hydrogen and found it to be ineffective. We have also tried regenerating the catalyst by passing pure oxygen over it and at the same time exposing it to low power illumination. This technique worked quite well as indicated by the fact that when the catalyst was so regenerated, it was restored to the same activity observed with an unused catalyst sample. We have used this regeneration technique during acquisition of most of the data presented below.

The reaction profile for hexane over 5% V_2O_5 on 13% Al_2O_3/SiO_2 was studied using helium as the carrier gas. With a carrier flow-rate of 10.2 cm^3/min , the concentration of reactant in the reactor effluent reaches a maximum at 1.1 min after injection. The principal products are methane (CH_4), ethylene (C_2H_4), and benzene (C_6H_6). The rate of production of benzene appears to be slightly lower than the rates of production of methane and ethylene. This can be seen most readily from a graph of weight percent of products as a function of the time after injection of the reactant. Such a graph is given in Figure 3. If all products were produced at the same rate, then the weight percent of each product would be constant, independent of reaction time. As one can see in Figure 3, the weight percent of ethene decreases while the weight percent of benzene increases with time. The time profile for the reactant hexane is shown by the dashed line. The major portion of reaction occurs between 0.8 and 1.3 minutes after injection of reactant. This will vary with carrier flow-rate

FIGURE 3. Product profiles for reforming reaction of n-hexane over V_2O_5 on an alumina-silica support and under high flux irradiation.

TABLE 3
EFFECT OF $V_2O_5/(13\%Al_2O_3-SiO_2)$ RATIO ON PHOTOCATALYTIC REFORMING OF HEXANE

Parameter	Parameter Value			
Reactant:	hexane*	hexane*	hexane*	hexane*
Reactant Formula:	n-C ₆ H ₁₄	n-C ₆ H ₁₄	n-C ₆ H ₁₄	n-C ₆ H ₁₄
Catalyst:	1% V ₂ O ₅	3% V ₂ O ₅	5% V ₂ O ₅	10% V ₂ O ₅
Catalyst Support:	13%Al ₂ O ₃ -SiO ₂	13%Al ₂ O ₃ -SiO ₂	13%Al ₂ O ₃ -SiO ₂	13%Al ₂ O ₃ -SiO ₂
Support Partical Size (μm):	60	60	60	60
Cat. + Sup. Weight (g):	0.0837	0.0823	0.0828	0.0818
Carrier Gas:	argon**	argon**	argon**	argon**
Carrier Flow Rate (cm ³ /min):	10.2	10.2	10.2	10.2
Sampling Time (min):	1.5	1.5	1.5	1.5
Lamp Electrical Input (W):	488.3	488.3	488.3	493
Lamp Optical Output (W):	14.2	14.2	14.2	14.3
Percent Conversion:	74.87	84.98	85.05	85

Reaction Product	Weight Percent Yield Under Above Conditions			
Methane (CH ₄)	23.74	25.48	25.08	26.31
Ethane (C ₂ H ₆)	2.77	2.94	2.79	2.25
Ethene (C ₂ H ₄)	40.89	43.43	42.55	46.54
Propane (C ₃ H ₈)	0.55	0.50	0.42	-
Propene (C ₃ H ₆)	7.10	7.06	6.09	5.32
isoButane (C ₄ H ₁₀)	1.85	1.65	1.39	-
Butane (C ₄ H ₁₀)	-	-	-	-
isoButene (C ₄ H ₈)	0.65	1.37	1.49	-
Butenes or Branched C ₅ 's	3.30	2.21	2.16	1.09
Benzene	19.09	15.89	18.67	14.8

* Data obtained using 1.5 μl pulsed injections of reactant.

** Catalyst bed was regenerated between each run by switching carrier gas to pure oxygen at 30 cm³/min.

and reactor temperature.

In order to evaluate the effect of catalyst parameters, the reaction products were measured at a specific reaction time in the vicinity of the point at which their concentration in the reactor effluent is maximum. This not only conserves time, but also reduces the number of samples to which the catalyst is exposed and assures that comparisons are made at constant catalytic activity. This data can be used to evaluate the effect of the parameters on the specificity of the reaction towards the desired product, benzene, but does not give any direct information about the effects the parameters have on reaction rate. The closest measure of the effect on reaction rate is the percent conversion which is given in all the data tables discussed below.

In our initial experiments, we used helium as the carrier gas and various Al_2O_3 - SiO_2 mixtures as catalyst supports. Generally the yields of benzene were low (~5 to 6 %) and the catalyst activity decreased with use, apparently due to carbon build-up on the catalyst/support surface. As mentioned above, catalyst activity could be restored by removing this carbon by reaction with oxygen in the presence of low power radiation.

In these preliminary studies, it was also noted that the benzene yield depended greatly on the carrier gas used, helium or argon. Greater yields of benzene were produced and at lower optical input power when argon was used. We believe this is due to the great difference in thermal conductivity of these gases, but subsequent studies are needed to confirm this.

In Table 3, the effect of V_2O_5 loading (from 1% through 10% V_2O_5 by weight) on 13% Al_2O_3 - SiO_2 is shown. Note that the percent benzene yield varies somewhat from 15 to 19% without any definite trend within experimental error. The total percent reactant conversion, however, increases from 75% to 85% in going from 1% to 3% V_2O_5 and then remains constant as the V_2O_5 loading is further increased to 5% and 10%. This data suggests that a V_2O_5 loading of 3% is satisfactory.

In Table 4, the effect of the ratio of Al_2O_3 to SiO_2 in the catalyst support is shown for a constant V_2O_5 loading of 3%. The benzene yield is obviously greatest when a pure SiO_2 support is used. This was also true at V_2O_5 loadings of 1% and 5%.

In Table 5, the effect of V_2O_5 loading (from 1% through 5% V_2O_5 by weight) on pure SiO_2 is shown. Both the percent benzene yield (> 50%) and the percent reactant conversion (~95%) are high at loadings of 3% and above, but the range of loadings will have to be extended in order to

TABLE 4
EFFECT OF CATALYST SUPPORT ON V₂O₅ PHOTOCATALYTIC REFORMING OF HEXANE

Parameter	Parameter Value		
Reactant:	hexane*	hexane*	hexane*
Reactant Formula:	n-C ₆ H ₁₄	n-C ₆ H ₁₄	n-C ₆ H ₁₄
Catalyst:	3% V ₂ O ₅	3% V ₂ O ₅	3% V ₂ O ₅
Catalyst Support:	25% Al ₂ O ₃ /SiO ₂	13% Al ₂ O ₃ /SiO ₂	pure SiO ₂
Support Partical Size (μm):	65	60	75-88
Cat. + Sup. Weight (g):	0.0813	0.0823	0.0833
Carrier Gas:	argon**	argon**	argon**
Carrier Flow Rate (cm ³ /min):	10.2	10.2	10.4
Sampling Time (min):	1.5	1.5	1.5
Lamp Electrical Input (W):	492	488.3	493
Lamp Optical Output (W):	14.3	14.2	14.3
Percent Conversion:	71	84.98	96

Reaction Product	Weight Percent Yield Under Above Conditions		
Methane (CH ₄)	22.35	25.48	25.30
Ethane (C ₂ H ₆)	2.72	2.94	1.64
Ethene (C ₂ H ₄)	41.89	43.43	14.17
Propane (C ₃ H ₈)	-	0.50	-
Propene (C ₃ H ₆)	8.12	7.06	1.42
isoButane (C ₄ H ₁₀)	1.64	1.65	1.2
Butane (C ₄ H ₁₀)	-	-	-
isoButene (C ₄ H ₈)	1.45	1.37	-
Butenes or Branched C ₅ 's	2.26	2.21	0.64
Benzene	21.09	15.89	55.61

* Data obtained using 1.5 μl pulsed injections of reactant.

** Catalyst bed was regenerated between each run by switching carrier gas to pure oxygen at 30 cm³/min.

determine the optimum value. However, a benzene yield in excess of 50% is very impressive.

The data in Tables 3-5 were obtained using a constant radiant power of ~14.3 watts (~490 watts electrical input to the lamp). The effect on benzene yield and total reactant conversion produced by varying the radiant flux intensity is shown in Table 6 for 3% V₂O₅/SiO₂ (argon carrier). Note that the benzene yield increases, but the percent conversion decreases as the power is decreased. At 493 watts electrical input to the lamp, the benzene yield is 55% and the percent total reactant conversion is 96%. At 380 watts electrical (~11.1 watts optical), the benzene yield is in excess of 60%, but the percent conversion is only 61%.

For comparison, data as a function of lamp power for the reaction over 3% V₂O₅/SiO₂ using helium as the carrier gas are given in Table 7. Note that, in this case, at 490 watts electrical the benzene

TABLE 5
EFFECT OF V₂O₅/SiO₂ RATIO ON PHOTOCATALYTIC REFORMING OF HEXANE

Parameter	Parameter Value			
Reactant:	hexane*	hexane*	hexane*	hexane*
Reactant Formula:	n-C ₆ H ₁₄	n-C ₆ H ₁₄	n-C ₆ H ₁₄	n-C ₆ H ₁₄
Catalyst:	1% V ₂ O ₅	3% V ₂ O ₅	5% V ₂ O ₅	10% V ₂ O ₅
Catalyst Support:	SiO ₂	SiO ₂	SiO ₂	SiO ₂
Support Partical Size (μm):	73-88	75-88	75-88	75-88
Cat. + Sup. Weight (g):	0.0823	0.0833	0.0832	0.0826
Carrier Gas:	argon**	argon**	argon**	argon**
Carrier Flow Rate (cm ³ /min):	10.4	10.4	10.3	10.
Sampling Time (min):	1.5	1.5	1.5	
Lamp Electrical Input (W):	493	493	491	498
Lamp Optical Output (W):	14.3	14.3	14.3	
Percent Conversion:	95	96	95	87.5

Reaction Product	Weight Percent Yield Under Above Conditions			
Methane (CH ₄)	35.32	25.30	24.01	26.7
Ethane (C ₂ H ₆)	2.00	1.64	1.36	1.81
Ethene (C ₂ H ₄)	20.92	14.17	12.66	44.75
Propane (C ₃ H ₈)	-	-	-	-
Propene (C ₃ H ₆)	1.98	1.42	1.35	4.40
isoButane (C ₄ H ₁₀)	1.50	1.2	1.09	1.85
Butane (C ₄ H ₁₀)	-	-	-	-
isoButene (C ₄ H ₈)	-	-	-	-
Butenes or Branched C ₅ 's	0.87	0.64	2.66	2.15
Benzene	37.38	55.61	56.83	17.61

* Data obtained using 1.5 μl pulsed injections of reactant.

** Catalyst bed was regenerated between each run by switching carrier gas to pure oxygen at 30 cm³/min.

TABLE 6
EFFECT OF RADIANT POWER ON 3%V₂O₅/SiO₂ with HELIUM CARRIER GAS

Parameter	Parameter Value		
Reactant:	n-hexane*	n-hexane*	n-hexane*
Support Partical Size (μm):	75-88	75-88	75-88
Cat. + Sup. Weight (g):			
Carrier Gas:	argon**	argon**	argon**
Carrier Flow Rate (cm ³ /min):			
Sampling Time (min):			
Lamp Electrical Input (W):	493	393	380
Percent Conversion:	96	80	61
Benzene Yield (Wt. % of Prod.)	55	61	63

* Data obtained using 1.5 μl pulsed injections of reactant.

** Catalyst bed was regenerated between each run by switching carrier gas to pure oxygen at 30 cm³/min.

TABLE 7
EFFECT OF RADIANT POWER ON 3%V₂O₅/SiO₂ with ARGON CARRIER GAS

Parameter		Parameter Value	
Reactant:	n-hexane*	n-hexane*	n-hexane*
Support Partical Size (μm):	75-88	75-88	75-88
Cat. + Sur. Weight (g):			
Carrier Gas:	helium**	helium**	helium**
Carrier Flow Rate (cm ³ /min):			
Sampling Time (min):			
Lamp Electrical Input (W):	490	591	753
Percent Conversion:	15	44	86.5
Benzene Yield (Wt. % of Prod.)	80	54	38

* Data obtained using 1.5 μl pulsed injections of reactant.

** Catalyst bed was regenerated between each run by switching carrier gas to pure oxygen at 30 cm³/min.

yield is 80%, but the total reactant conversion is only 15%. As the lamp power is increased the percent conversion increases, but the percent benzene yield decreases. For a given percent conversion, the percent benzene yield is higher when argon is used as the carrier than when helium is used.

For the reforming of hexane to benzene using V₂O₅/SiO₂, catalyst regeneration using oxygen appears to be especially effective when the regeneration is done with the catalyst/support system exposed to low power radiation from our lamp. When radiation is used, we note that the carbon formed during exposure to hexane is very rapidly removed from the upper surface of the catalyst bed, the surface exposed to the radiation. The lower part of the bed is regenerated more slowly, as the particles in this region rise to the illuminated top surface. During the regeneration cycle, we use oxygen flow rates that are sufficient to fluidize the bed and carbon removal appears to be complete in 2-3 minutes. However, in order to be certain that regeneration is complete we continue the process for a total of 20 minutes. This regeneration step is normally done during the 40 minute period required for gas chromatographic analysis of a reaction product sample. The effectiveness of radiation for catalyst regeneration may well be one of the most important advantages of using radiant energy input for heterogeneous catalyzed reactions. For this reason, we will carry out a quantitative comparison of the rates of catalyst deactivation and regeneration produced by thermal and radiant energy.

1988 EXPERIMENTAL WORK

Studies for optimization of reaction and catalyst parameters for the production of benzene from hexane will be continued. The range of V_2O_5/SiO_2 ratios will be extended. The dependence of benzene yield on optical power will be further investigated.

After optimization of the parameters for benzene formation from hexane, the reforming of other aliphatic hydrocarbons (C_1 to C_{10}) to aromatic compounds, typically toluene and xylenes, will be evaluated. The dependence of these reactions on the ultraviolet region of the input spectrum will also be measured.

Following this work, the reactions proposed above in the section titled "Candidate Chemical Reactions" will be tested to see if higher value substituted aromatics can be produced using high flux radiation and V_2O_5 catalysts. In general these reactions involve a combination of two reactants. One approach would be to use hexane as one of the reactants with the anticipation that substitution would occur during the formation of benzene. Alternatively, benzene could be used as one of the reactants with the assumption that substitution can occur directly to the existing aromatic ring.

EXPECTED OUTCOME OF 1988 EXPERIMENTAL WORK

We are optimistic that the benzene yield from hexane can be increased significantly. To date the greatest benzene yield achieved is 57% at 97% total reactant conversion. This was obtained using 5% V_2O_5 on a pure SiO_2 support. We expect to be able to achieve a benzene yield in excess of 65% at a total reactant conversion in excess of 90% under optimum conditions.

We also are confident that other substituted aromatics can be produced using high flux radiation and V_2O_5 catalysts. This will be demonstrated definitively. These reactions will be tested for a wavelength dependent photocatalytic effect by the method described above. It is not possible to predict the outcome of these experiments at the present time. The production of substituted aromatics by combination reactions between two reactants will also be attempted and, if successful, tested for a wavelength dependent photocatalytic effect. Again, the outcome cannot be predicted with certainty. However, if a photocatalytic effect can be found we believe that this would be of considerable commercial significance since the target products, substituted aromatics, have a relatively high dollar value.

The most critical limitation to the present study is the inability to investigate the spectroscopic properties of our catalyst/support systems at high temperatures. Other workers (see Appendix) have identified a unique photocatalytic excited electronic state of V_2O_5 , i.e. the state produced by the charge transfer $V^{5+}O^{2-} \rightarrow V^{4+}O^-$. They have studied both the absorption and emission properties of this species at room temperature using a low photon flux. However, when we use high photon flux the catalyst is at a much higher temperature, where the spectroscopic properties are unknown. Furthermore, when we prepare new catalysts or attempt to regenerate old catalysts, effectiveness can only be judged by reaction activity. If the spectroscopic properties could be determined directly, we could evaluate alterations in the electronic states responsible for photocatalytic activity.

Another limitation is the method of product detection used in our present analytical procedure. Presently we are using gas chromatography to identify the reaction products and to measure concentrations, which is a time consuming process. We believe productivity would be greatly increased by the use of an ion-trap mass spectrometer. A proposal for \$177,900 has been submitted to the U.S. Department of Energy, University Research Instrumentation Program, for purchase of such equipment.

PRESENT VIEW - PROCESS PATHS & CONFIGURATIONS

Research objectives 4) and 5) on p3, i.e. photo-catalytic reactor configuration, and the integrated process sequence, provide the basis for our present view of the process configuration for a pilot-scale and commercial-scale unit.

The point has been made that for a cost effective process operation the equipment should be operated 24 h/d, an endothermic photo-catalytic reaction during day-time, and an exothermic reaction using the same catalyst during night-time. To this end, one can visualize a combination of reaction paths from feedstocks to high \$-value products, as shown in Figure 4, which accomplish these objectives. More specifically the three reaction paths can be visualized as follows.

The first path (PMCA), combines paraffins + methanol to aromatics + cresols (day-time), followed by air oxidation (night-time) to benzaldehyde + other oxygenated products (unidentified at this time):

Figure 4. REACTION & PROCESS PATHWAYS

- Feedstocks to High Value Products -

[3-pathways: 1) PMCA, 2) AMCA, 3) PAA.]

The second path (AMCA), combines aromatics + methanol to cresols (day-time), followed by air oxidation (night-time) to other oxygenated products:

The third path (PAA), paraffins to aromatics via photo-catalysis (day-time), followed by air oxidation to maleic anhydride and benzaldehyde (night-time):

A "price Advantage Ratio", measuring the synthesis upgrading from feedstocks to products, can be estimated for each path, and is presented in the next section of this report.

Three (3) key points are pertinent in our current thinking about the process configurations:

1) The Process Unit would consist of a reactor plus a product separation unit, with provisions for recycle of unreacted material.

2) The catalytic reactor would be a shallow fluidized bed (height / diameter < 0.5) of V₂O₅ (~10-15w%) on microsphereoidal SiO₂-Al₂O₃ (~65 μ diameter) catalyst support particles.

3) The reactor would be computer controlled and time cycled (with over-ride) for day-time and night-time operation.

PRELIMINARY ECONOMICS - PRICE ADVANTAGE RATIOS

It is premature at this time to calculate comparative process economics of the proposed reaction-process paths. Later in the project sufficient experimental data will be available to prepare some preliminary process economics. However, at this time as an indicator, a "Price Advantage Ratio (Ra)" measuring the up-grading from feedstocks to products can be estimated for each proposed path.

Consider as an example the PAA process path, paraffins - aromatics - aldehydes. Making certain preliminary assumptions concerning selectivity and conversion, a mass balance can be made from reactants to products; followed by calculation of product value (\$) and feedstock cost, as illustrated by Table 8. In a

similar manner, Ra values have been calculated for the other two reaction-process paths, PMCA and AMCA, and the values summarized in Table 9. It is interesting to note that the simplest reaction path appears to have the highest up-grade ratio.

Another preliminary up-grading indicator, feedstocks to products, has been suggested as a measure; i.e. the value added, $V_a = \text{Products (\$)} - \text{Feedstocks (\$)}$. These values have been added to Table 9, and it will be noted that on the basis of V_a the AMCA path shows up best. However, starting with n-paraffins to aromatics, a very desirable step for the utilization of solar radiation, the PAA path is best on both bases.

Table 8. PRICE ADVANTAGE RATIO, PAA Path

<u>Compound</u>	<u>Feedstock</u>	<u>Products</u>	<u>Price</u>	<u>Value</u>
	(lbm)	(lbm)	(\$/lbm)	(\$)
n-paraffins	100.20	10.020	0.089	0.8918
toluene		6.313	0.190	1.1994
butenes		2.110	0.260	0.5485
hydrogen		5.959	0.152	0.9058
oxygen	27.939	2.794	0.024	0.0671
aldehyde		65.440	1.25	81.80
water		11.108	-0-	-0-
epoxides		24.401	0.475	11.59
	128.14	128.14		97.003

$$R_a = (97.003/9.588) = \underline{10.1} <---$$

Table 9. COMPARATIVE Ra and Va VALUES

<u>Reaction Path</u>	<u>Feedstock (\$)*</u>	<u>Products (\$)*</u>	<u>Ra</u>	<u>Va (\$)</u>
PAA	9.588	97.03	10.1	87.4
PMCA	10.85	90.23	8.32	79.4
AMCA	20.19	125.1	6.23	105.

* Basis: one lbmole of primary reactant

COMPARATIVE COMMERCIAL PROCESSES

There are a number of commercial processes which are used to produce the

chemical products envisioned. However, principally there are four (4) processes that are directly related to the paths proposed above; some brief comments about each follow.

1) Phillips Petroleum Company[11]: Process for Catalytic Dehydrocyclization and Dehydrogenation of Hydrocarbons. This fluid-bed thermal-catalytic, catalyst $V_2O_5-SiO_2$, process currently under development, has the objective of producing aromatics from n-paraffins for high octane motor gasoline blending stocks, as well as aromatics for chemical manufacture.

2) Spence & Sons [11]: Process for Synthetic Cresols by Alkylation of Phenol with Methanol. This catalytic (Al_2O_3) process can be operated in fixed-bed or fluid bed, at temperatures of 340-355°C.

3) Rhone-Poulenc S.A. [12]: Process for Benzaldehyde and Benzoic Acid by Oxidation of Toluene. This catalytic ($V_2O_5/SiO_2-Al_2O_3$) vapor phase air oxidation process can be operated in fixed- or fluid-bed, at a temperature of ~400°C, simultaneously producing the aldehyde and acid.

4) Shell Development Company [13]: Process for Epoxides by Direct Oxidation. This catalytic vapor phase oxidation process at 327°C in fixed- or fluid bed has conversions of 50-70 %, also producing some complete oxidation products, CO_2 and H_2O .

PRELIMINARY CONCLUSIONS

Based on the research accomplished to date, as summarized in this report, our preliminary conclusions are as follows:

1) As reported previously, we observed a significant photo-catalytic effect: increased conversion rate and selectivity, for the dehydration and dehydrogenation of alcohols. It is believe that excited state catalyst sites cause this enhancement.

2) n-Hexane reforming results indicated: high conversions (50-95%), greater olefin (than aromatic) yield at low V_2O_5 loading, and increased and greater aromatic (than olefin) yield for increased V_2O_5 loading. With 5w% V_2O_5 , 95 % conversion and 57% aromatics were obtained.

3) n-Heptane reforming should maximize toluene yield, which in turn could be either hydroxylated to cresol or oxidized to benzaldehyde; both of the latter are high \$-value products.

4) In order to produce a cost effective process, the odds-on-favorite pilot scale and commercial scale reactor configuration and operational sequence are: a shallow fluid-bed of catalyst with top-down incident radiation, and day-time

endothermic followed by night-time exothermic reactions to produce the products.

5) The Price Advantage or Up-Grade Ratio, R_a , can be used to rate alternative reaction-process paths, and consequently determine the priority of experimental work.

6) Finally at this time, the chances for success appear very good for the use of solar photo-thermal catalytic reactions to produce high value chemicals. This development of technology could significantly extend the cost effective application of solar energy for useful purposes.

. SELECTED REFERENCES .

- [1] F-M Lee, "Catalytic Dehydrocyclization-Dehydrogenation of Hydrocarbons" U.S. Patent #4,607,129 (1986).
- [2] 1987 Petrochemical Handbook, Hydrocarbon Processing, p59ff, Nov. 1987.
- [3] V.G. Mokerov, V.L. Makarov, V.B. Tulvinskii, and A.R. Begishev, Opt. Spectrosc., 40 (1), 58 (Jan 1976).
- [4] K.C. Polonczyk, Majid Saghafi, J.A. Wilking, and K.S. Kramer, Report: "Endothermic Photo-Catalytic Reactions", Chemical Engineering Department, U/Houston (1986 revised 1988).
- [5] S. Yoshida, Y. Matsumura, S. Noda, and T. Funabiki, J. Chem. Soc. Faraday Trans. 1, 77, 2237 (1981).
- [6] A.M. Gritskov, V.A. Shvets, and V.B. Kazanskii, Chem. Phys. Lett., 35, (4), 511 (1975).
- [7] V.A. Fenin, V.A. Shvets, and V.B. Kazanskii, Kinert. Katal., 20 (4), 952 (1979).
- [8] V.B. Kazanskii, Kinert Katal., 19 (2), 279 (1978).
- [9] S.L. Kaliaguine, B.M. Shelimov, and V.B. Kazanskii, J. Catal., 55, 384 (1978).
- [10] A. Masakazu, I. Tanahashi, and Y. Kubokawa, J. Phys. Chem., 86 (1), 1 (1982).
- [11] N.M. Cullinane and W.C. Davies, Brit.Pat., #600,837, 20 Apr 1948; ibid, Brit.Pat., #600,838, 20 Apr 1948; ibid, Brit.Pat., #602,257, 24 May 1948.
- [12] J. Bonnart and G. Poilane, U.S. Pat. #3,387,036, 4 June 1969; J.C. Brunie, U.S. Pat., #3,658,875, 25 Apr 1972; M. Jouffret, U.S. Pat, #3,948,995, 6 Apr 1976.
- [13] Shell Development Company, U.S. Pat., #3,119,837, (1964).
- [14] G.V. Samsonov, The Oxide Handbook, second edition, IFI Plenum (1982).

APPENDIX

LIGHT SOURCE - In this research, the emission from a high pressure xenon arc lamp is used to provide the radiant input energy to a reactor. Two lamp systems have been purchased, installed, and characterized. The smaller of the two (Photon Technology International Inc., Princeton, NJ, model 02-A1000 lamp housing and model 02-LPS 200 power supply) operates at a maximum electrical input power of 150 W. The larger (Photon Technology International Inc., Princeton, NJ, model 02-A5000 lamp housing and model 02-A5001 power supply) operates at a maximum electrical input power of 1000 W. With each system, the electrical input power can be varied to produce a proportional variation in the optical output power. The use of a xenon lamp requires that both of the lamp housings be mounted so that their optical axis is horizontal. In order to provide the vertical beam axis required for the reactor designs selected (see below), a front surface, plane mirror has been used with each lamp to provide a 90° deflection of the emitted light beam. Each lamp housing includes a high precision elliptical mirror which focuses the emission from the arc lamp into a very small spot of high flux density radiation. The flux density distribution of the emission in the vicinity of the focus for each lamp system has been measured using an asymptotic calorimeter (HY-CAL model C-1300-A-300-072). For the 1000 W system, including mirror and operated at maximum power, the maximum flux density measured on a 1.27 mm diameter surface located at the focal point is 131.65 W/cm² and the total flux on a 6 mm diameter circular surface is 25.55 W. For the 150 W system, including mirror and operated at maximum power, the maximum flux density measured on a 1.27 mm diameter surface located at the focal point is 9.38 W/cm² and the total flux on a 2 mm diameter circular surface is 0.28 W. In each case the radial flux density distribution is approximately gaussian. Three axis mounting tables are used to position reactors so that the catalytic surfaces contained are located at the focal points of each lamp system.

SELECTION OF POTENTIAL PHOTOCATALYSTS - A survey of the available chemical literature has convinced us that vanadium pentoxide (V₂O₅) is a catalyst which is very likely to provide the photocatalytic activity desired. It has been reported⁵ that V₂O₅ supported on silica (SiO₂) is photocatalytic with respect to the oxidation of carbon monoxide (CO). The electronic states involved have been identified by spectroscopic measurements⁶. An optical absorption band for V₂O₅/SiO₂ occurs in the 313-370 nm range. The wavelength dependence of the quantum yield for oxidation of CO to CO₂ also shows a maximum in this range. This absorption band falls within the sea level solar spectrum. When V₂O₅/SiO₂ is excited by radiation in this absorption band, phosphorescence is observed in the region 435-590 nm (maximum at 525 nm). The phosphorescence arises from a T₁ → S₀ transition. Since this is a forbidden transition, the triplet (T₁) state is relatively long lived. As is well known in photochemistry, long-lived triplet states are most

amenable to photochemical reaction.

The support used with V_2O_5 appears to have a very significant effect on its photocatalytic properties⁵. When V_2O_5 is supported on silica or on porous vicor glass (PVG), photocatalytic oxidation of CO is observed. When V_2O_5 is supported on alumina, photocatalytic oxidation of CO is not observed.

Reaction of CO with triplet V_2O_5 is further supported by studies of the reaction using V_2O_5 /PVG. The spectroscopic properties of V_2O_5 /PVG are slightly different from those for V_2O_5 /SiO₂. For V_2O_5 /PVG, the absorption band has a maximum at 290 nm and the emission consists of both a fluorescence band (maximum at 360 nm) and a phosphorescence band (maximum at 500 nm, mean lifetime 218 μ sec). With CO adsorbed, two phosphorescence lifetimes were observed: 218 μ sec, and 522 μ sec. It was proposed that two mechanisms were responsible for the quenching of the triplet state by CO: (1) collisional quenching and (2) quenching due to adsorption. Although V_2O_5 /PVG would also appear to be a potential photocatalyst for our experiments, its potential is limited by the fact that its absorption band is barely within the solar spectrum.

The spectroscopic properties of V_2O_5 supported on magnesia (MgO) have also been investigated⁷. For V_2O_5 /MgO, the absorption band has a maximum at 340 nm and the emission is phosphorescence (maximum at 580 nm). The absorption band extends to ~390 nm which is well within the sea level solar spectrum.

In all of these cases the optical absorption band is considered to be associated with a charge transfer from O^{2-} to V^{5+} giving $V^{4+}O^-$ as the excited state. Thus, it is understandable that V_2O_5 would be effective as a photocatalyst for converting CO to CO₂. There are other reports of photocatalysis using V_2O_5 . Some of these identify free radical species formed in the photocatalytic process^{8,9}. With hydrocarbons this frequently involves a hydrogen atom abstraction by O^- in the charge transfer excited state ($V^{4+}O^-$) to form OH^- .

Spectroscopic and photocatalytic studies have also been reported for the catalyst/support combinations MoO₃/SiO₂, MoO₃/PVG, and CrO₃/PVG¹⁰. In these systems, triplet states can be excited using radiation in the vicinity of 300 nm. However, for both MoO₃/PVG and CrO₃/PVG the lifetimes of these states are shorter than for V_2O_5 /PVG. Consequently, V_2O_5 /PVG should be more effective as a photocatalyst than either MoO₃/PVG or CrO₃/PVG. This assumption is borne out by the fact that V_2O_5 /PVG gives a higher quantum yield for conversion of CO to CO₂ than either MoO₃/PVG or CrO₃/PVG. The metal oxides NiO, Co₃O₄, Cr₂O₃, Fe₂O₃, and CuO were also

investigated. None of these exhibited photocatalytic activity with CO.

In sum these studies suggest that V_2O_5 (on a variety of supports including silica, magnesia, and porous vicor , but not alumina) is a very appropriate candidate for use in the present research. When combined with these supports, it has a measured absorption band which falls within the solar spectrum and exhibits photocatalytic activity for at least one chemical reaction. It is also a catalyst which is commonly used in a wide variety of commercially important chemical syntheses. For this reason, we have chosen to concentrate on applications of this catalyst.

Document Control Page	1. SERI Report No. SERI/TP-253-4275	2. NTIS Accession No. DE91002140	3. Recipient's Accession No.
4. Title and Subtitle Solar Photo-Thermal Catalytic Reactions to Produce High Value Chemicals			5. Publication Date April 1992
			6.
7. Author(s) H.W. Prengle, Jr., W.E. Wentworth			8. Performing Organization Rept. No.
9. Performing Organization Name and Address University of Houston 4800 Calhoun Houston, Texas 77004			10. Project/Task/Work Unit No.
			11. Contract (C) or Grant (G) No. (C) XX-7-07028-1 (G)
12. Sponsoring Organization Name and Address Solar Energy Research Institute 1617 Cole Boulevard Golden, Colorado 80401-3393			13. Type of Report & Period Covered Technical Report
			14.
15. Supplementary Notes SERI Technical Monitor: R. Gerald Nix, (303)231-1757			
16. Abstract (Limit: 200 words) This summarizes research about how solar photo-thermal energy can convert low cost chemical feedstocks to high dollar-value chemical products. Chemical market analysis and product price distribution focused on specialty chemicals with prices greater than \$1.00/lb, and a synthesis sequence of n-paraffins to aromatics to partial oxidized products. It was demonstrated that enhanced reaction effects result from VIS-UV irradiation of catalytically active V_2O_5/SiO_2 . Experiments involved dehydrogenation and dehydrocyclization of n-paraffins to olefins and aromatics, the latter was preferred. Results using n-hexane produced 95% conversion with 56% benzene; aromatic yield might reach ~70% by further optimization. Pilot- and commercial-scale reactor configurations were examined; a shallow fluid-bed of catalyst with incident radiation from the top was favored. Daytime endothermic followed by nighttime exothermic reactions would be most cost-effective.			
17. Document Analysis a. Descriptors Photothermal catalytic reactions; high value chemicals; synthesis products; hydrocarbon reforming reactions b. Identifiers/Open-Ended Terms c. UC Categories 248			
18. Availability Statement National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			19. No. of Pages 33
			20. Price A03

END

**DATE
FILMED**

7 / 8 / 92