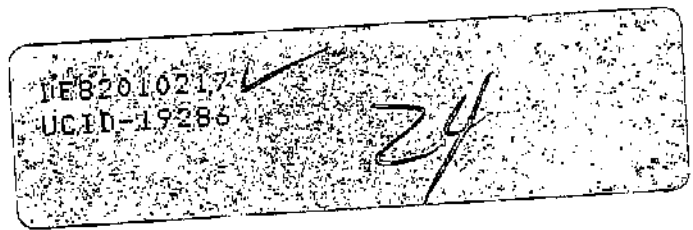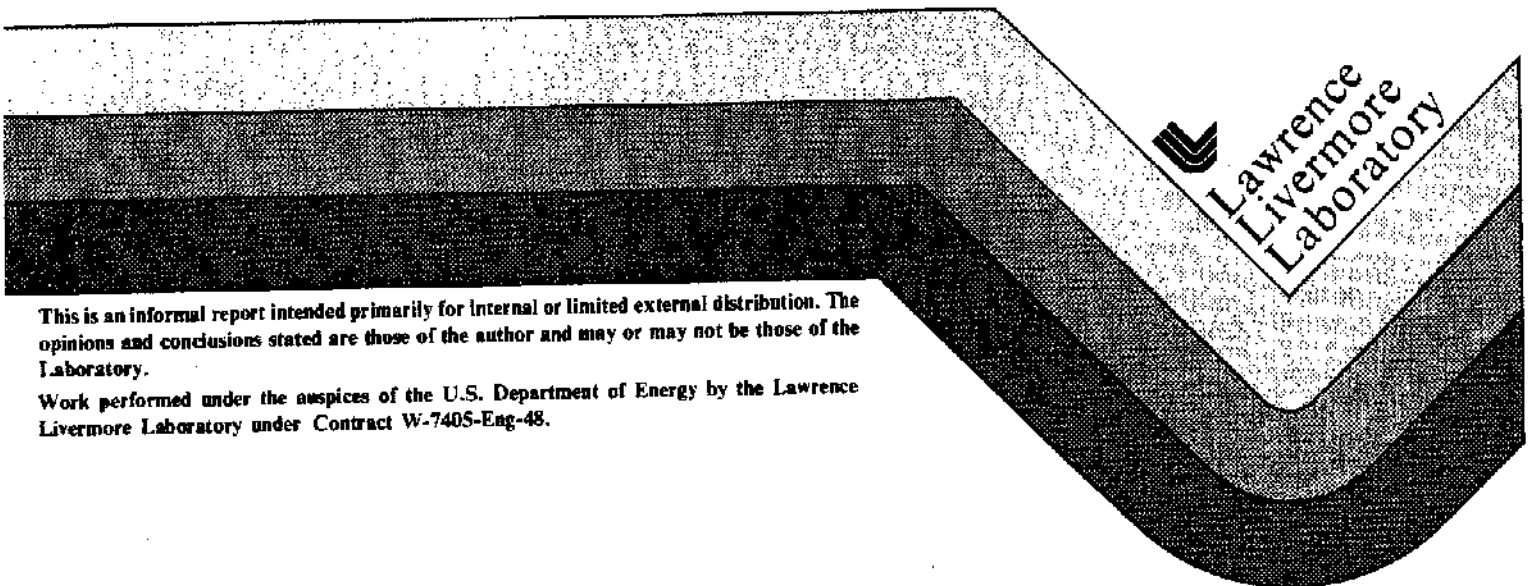063044

DEVELOPMENT OF A DEMONSTRATION REACTOR USING THORIA AS A FISCHER-TROPSCH CATALYST

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We have demonstrated experimentally that thorium oxide may be used as a catalyst with CO + H_2 mixtures to produce either methanol or a mixture of hydrocarbons from C_1 to C_5 (saturated and unsaturated). The immunity of ThO_2 to poisoning by sulfur compounds makes its use very attractive for industrial applications. We are proposing to optimize the experimental conditions of the catalytic process using a one-inch reactor and to scope and define the experimental conditions for a pilot plant demonstration.

1. INTRODUCTION

A large number of the solid catalysts used in catalytic reactions to produce hydrocarbons and alcohols from synthesis gas are based on the transition metals, notably Fe, Ru, Ni, Rh, Zn, and Cu. These metals all have unfilled inner electron shells (3d, 4d, 5d) protected by outer s-shell electrons. Similar electron configurations are found in the actinide series in which thorium has unfilled 5f levels, while in uranium the 5f, 6d and 7s shells are so close together that hybridization of the 5f and 6d electrons has been observed. These electron configurations suggest that thorium and uranium should have useful catalytic properties. The literature search by Bastasz and Colmenares[1] has shown this to be the case. Thorium is particularly attractive because it has a very stable oxide composition (ThO_2), whereas uranium oxides can easily change in stoichiometry and thus require an over-pressure of oxygen to maintain stable compositions. Interestingly enough, most of the significant work on thorium has been done outside the United States.

Thorium dioxide has been used as an additive for the so-called "standard" cobalt Fischer-Tropsch catalyst for the synthesis of hydrocarbons from mixtures of CO and H_2. Its effect has been to increase the average chain length of the hydrocarbons produced on this catalyst.[2] Thorium dioxide has also been described as the "best single component catalyst" for carrying out the synthesis of branched hydrocarbons,[3] particularly the iso-C_4's. Branched hydrocarbons are particularly suited for use in motor fuels because of their antiknock characteristics; the iso C_4's are important because they are easily dimerized to iso-octane.[4]

One of the factors affecting the economic use of all currently utilized Fischer-Tropsch catalysts is sulfur poisoning which has made it necessary to reduce the sulfur content of synthesis gas mixtures to $\leqslant 4$ ppb.[5] Within the equilibrium system comprised of sulfur containing compounds, H_2-CO mixtures, and ThO_2, the formation of thorium sulfides is thermodynamically prohibited*; this has been experimentally demonstrated.[2] Approximately

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*$ThO_2 + 2H_2S \rightarrow ThS_2 + 2H_2O$ $\Delta G_{500-800^\circ K} = +37 kcal/mole$
$ThO_2 + CS_2 \rightarrow ThS_2 + CO_2$ $\Delta G_{500-800^\circ K} = +20 kcal/mole$
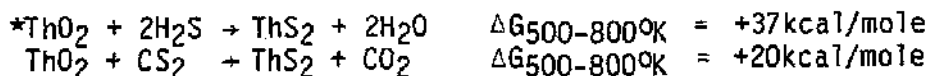
10% of the $1-4 billion cost of a medium size coal gasification plant is invested in sulfur removal[6a,b,c,d] from the synthesis gas, and a similar percentage of the plant operating cost is involved in catalyst replacement.[6a,b,c,d] Thoria's immunity to sulfur poisoning, leading to the relaxation on the purity requirements on the synthesis gas, and thus the elmination of sulfur removing processes, may mean that it will have economic advantages over catalysts in current use.

At the time the preliminary research on ThO_2 catalysts was done,[2,3] the high cost and relative scarcity of thorium made large scale utilization of this catalyst unfeasable. With the advent of processes to convert coal to gaseous and liquid fuels, and the development of a substantial reserve of cheap thorium (see Table I), it is appropriate to reconsider utilization of thoria as a catalyst.

Table 1. Cost (1979 dollars) of metals for Fischer-Tropsch catalysts.[7]

Material	Cost per pound($)
Iron	0
Potassium	24
Ruthenium	1820
Thorium*	10

*Approximately 3000 tons available from current domestic stockpiles.[8]

Approximately 300,000 tons in recoverable resources in U. S.[9]

2. RESULTS OBTAINED AT LLNL

Experiments utilizing a copper lined differential flow reactor, illustrated in Figures 1 and 2, have been carried out at low CO conversion ($\leqslant 0.1$ mole %) in order to determine the methanation rate over a catalyst with a known surface area under conditions that minimize effects due to the recombination of reactive species. These experiments have established a basis for comparing the performance of thoria with other catalysts.* Copper

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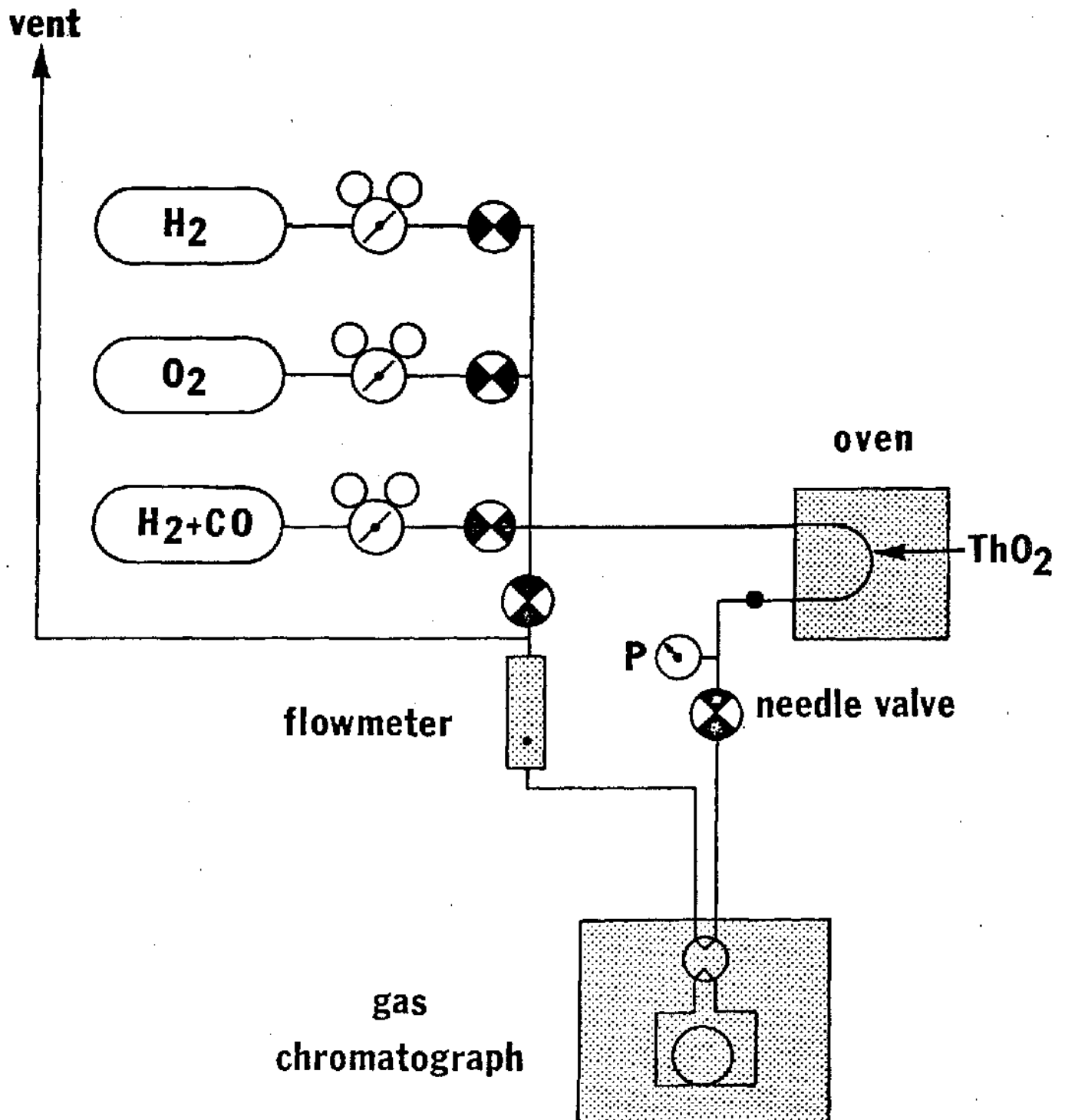*This type of information is not available in the early German work.

FIGURE 1.   EXPERIMENTAL EQUIPMENT

Catalyst bed

Thermocouple

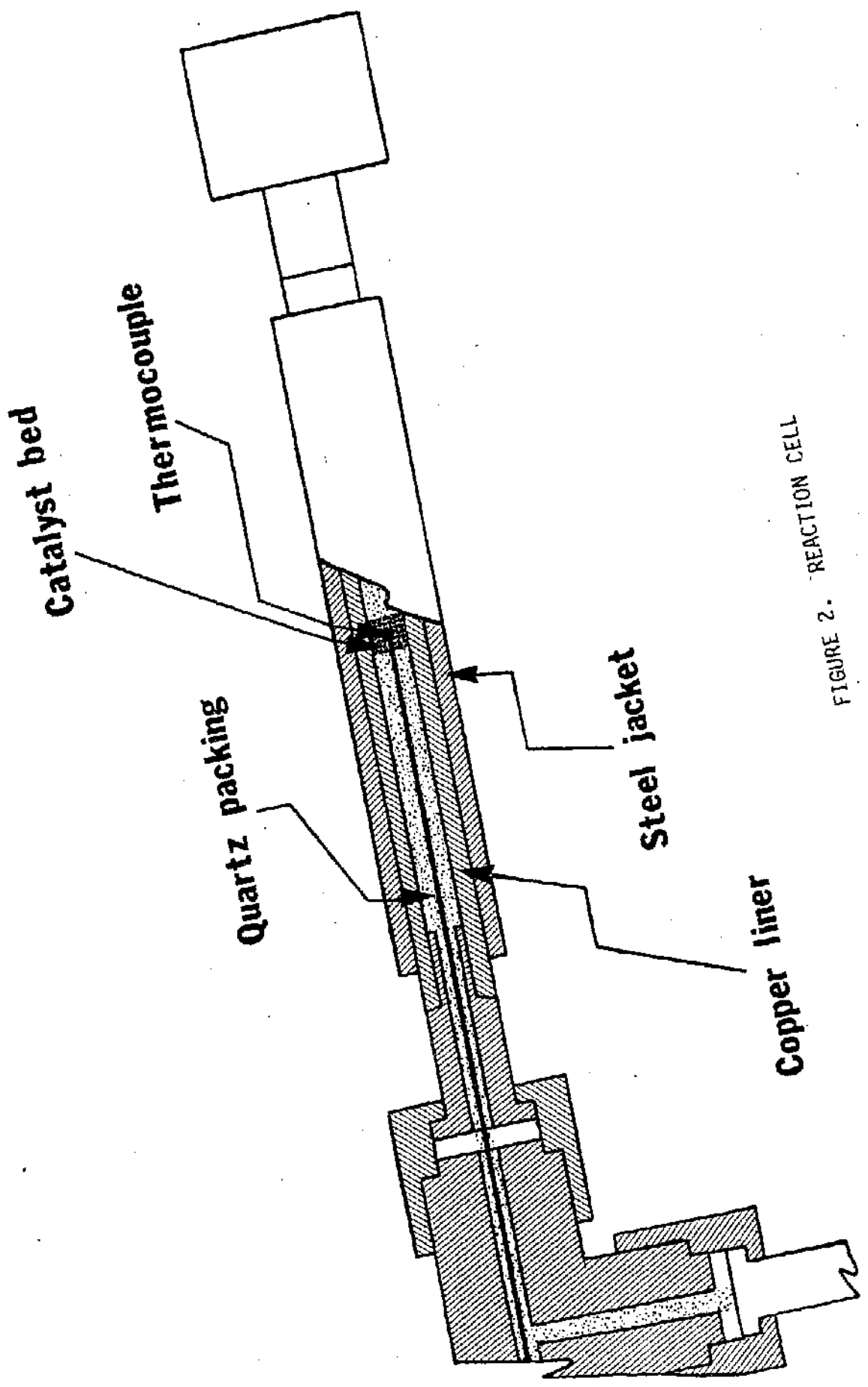Quartz packing

Steel jacket

Copper liner

FIGURE 2. REACTION CELL

was chosen as a liner material because the metal and its oxides are not catalytically active with H_2 + CO gas mixtures. The pressure of the CO + H_2 mixtures was held constant at 30 atmospheres, and the flow rate of effluent gases was maintained at 55 STD cc/min over 0.1 to 0.3 grams of catalyst. The surface area of the ThO_2 was determined to be approximately 1.3 m^2/g by a BET analysis. Experiments performed with the copper lined reactor and quartz filler material without a catalyst charge established that neither component was an active contributor to the reactions described below.

The variation in the product distribution for a 1:1 mixture of H_2/CO as a function of temperature is summarized in Table II. At low temperatures

Table II. Product distribution data for 1:1 CO to H_2 at 30 atm as a function of temperature. For ~0.1 mole% conversion.[2]

T^{o}C	CH$_3$OH	C$_1$	C$_2$ (%=)*		C$_3$	iC$_4$	C$_4$	C$_5$+
			Weight percent					
380	95.6	2.9	0.7	(86)	0	0.4	0	0.3
430	95.1	2.8	0.5	(80)	0	0.8	0.1	0.7
480	52.1	31.1	3.3	(70)	1.7	7.6	0.5	3.5
530	0	62.7	8.7	(63)	9.9	15.4	1.1	2.0
580	0	65.4	10.9	(62)	8.4	12.5	1.1	1.7

*(%=) = relative percentage of ethylene in this group.

methanol was the dominant product. As the temperature was increased, the percentage of methanol in the product stream decreased and methane became more abundant. Higher hydrocarbon production also increased with temperature with the percentage of C_3 and C_4 products reaching a maximum around 530°C. The relative precentage of ethylene decreased as a function of increasing temperature.

A partial comparison of the operating parameters for thoria and the more commonly used Fischer-Tropsch catalysts is given in Table III. These results

represent low CO conversion (≤0.1 mole %) and their purpose is to show that thoria exhibits a catalytic activity of the same order of magnitude as the other catalysts. The comparison of catalysts is based on their ability to produce methane even though this may not be the most desirable product. Methanol and C_2-C_5^+ hydrocarbons are more desirable products within the framework of the U. S. current fuel problems.

Table III. Comparison of performance of various Fischer-Tropsch catalysts.

Catalyst	Wt% CH_4	r_{CH_4} (molecule/ site*-sec.)	$E_A(CH_4)$ (kcal/mole)	T (°C)	p (atm)	H_2:CO	Reference
ThO_2	59	0.020**	21	530	30	1:1	10
Ru	62	0.181	24	275	1	3:1	11
Fe	67	0.06	21	275	1	3:1	11
Ni	90	0.03	25	275	1	3:1	11
Rh	87	0.01	24	275	1	3:1	11
Pd	95	0.01	20	275	1	3:1	11

*1 site = 1 unit cell of surface area $\cong$ 31 $Å^2$.

**8×10^{-6} mole/gm ThO_2/min.

Our laboratory is already equipped to carry out most of the experiments necessary to establish operating parameters for synthesis reactions over thoria catalysts, and to characterize the catalyst at various stages of preparation and consumption using modern surface analysis instrumentation. Carefully controlled, low-conversion experiments (≤0.1 mole percent) suggest that methanol, methane, and other hydrocarbons are produced at specific rates (i.e., number of molecules produced/unit cell of catalyst surface/second) that are competitive with similar reactions on Fe, Ru, Co, etc. An activation energy of ~21 ± 3 kcal/mole has been measured for the methanation reaction over ThO_2 between 450 and 550°C. The ability to operate the synthesis

reactions at high temperatures prevents buildup of waxy and/or resinous material in the reaction vessel while the high pressure shifts the thermodynamic equilibrium to favor the production of heavier hydrocarbons. Another factor affecting the economy of the synthesis over ThO_2 is the low ratio of H_2 to CO required to maintain a favorable product distribution. Roughly one part H_2 (the most expensive ingredient) is required per part CO, whereas most other catalysts operate with H_2:CO ratios from 2:1 to 4:1. To provide these higher ratios, various types of chemical reactors are necessary to process separately part of the coal gasifier output.

We believe that the German[2,3] work plus our own work at LLNL have demonstrated amply the scientific feasibility of using ThO_2 as a Fischer-Tropsch catalyst. A catalytic reactor using thoria may be installed directly to the output of most current coal gasifiers because they operate at pressures near 50 atmospheres and temperatures close to 1000^0C or higher.*[12,13] By operating in this fashion, sulfur compound removal and gas compression are eliminated thus further reducing capital and operating costs. Therefore, future work should be aimed at developing a practical thoria catalyst and the optimum experimental conditions for its usage in a large pilot plant.

3. PROPOSED APPROACH

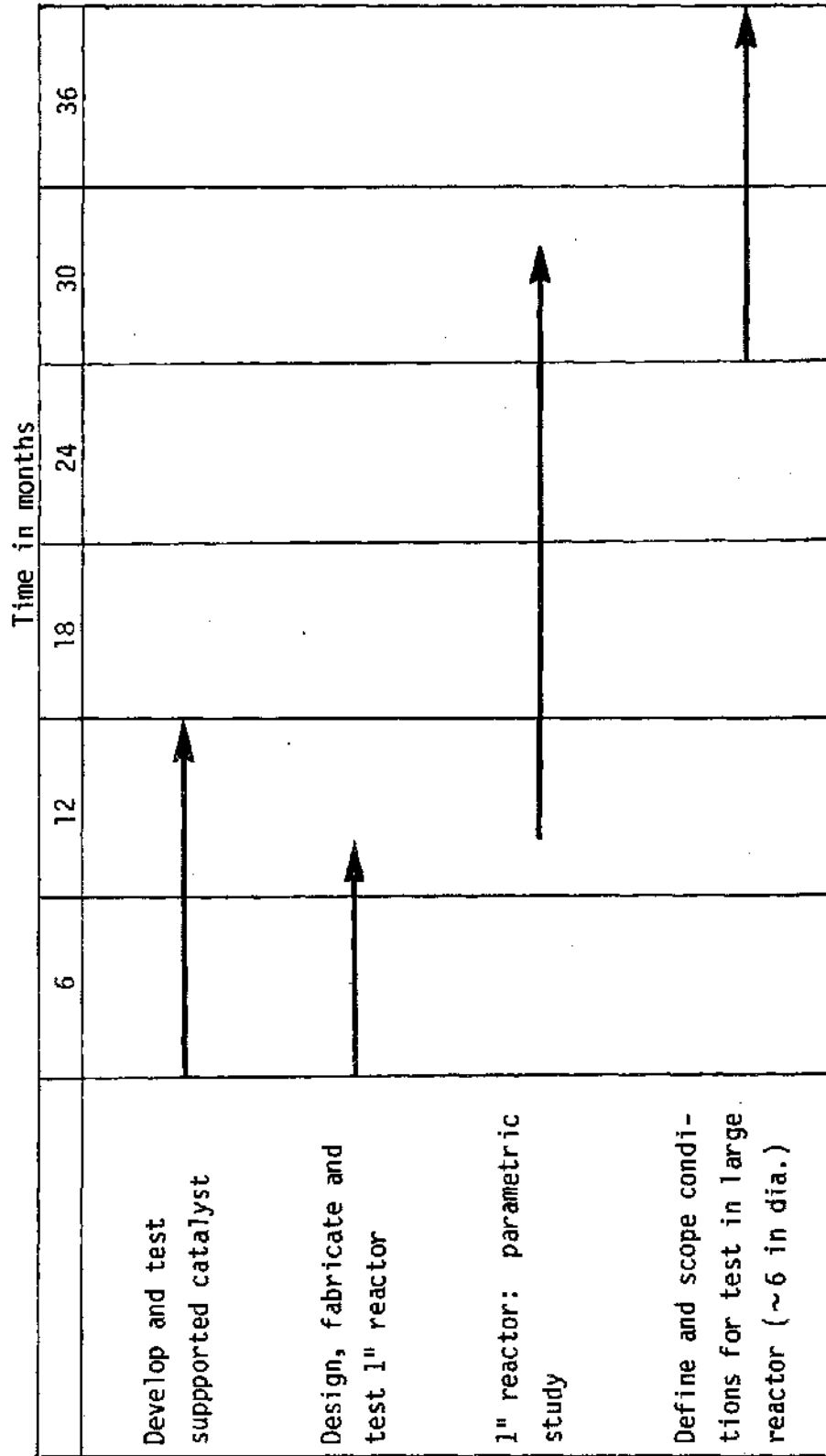We propose to develop a working reactor along the following lines:

A. Perform a statistically designed parametric study (i.e., Box-Behnken) using a 1" I.D. reactor to define optimum pressure (1-60 atm), temperature (350-550^{0}C), and H_2/CO ratio (0.5/1.0 to 4/1). These parameters will be investigated for low (≤ 0.1 mole%) to high conversions (~30-60 mole%). Low conversion experiments are needed to define basic catalyst performance in one single pass, without the complication of secondary and tertiary reactions taking place in large catalytic beds. High conversion experiments, on the other hand, will represent actual industrial conditions.

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*For example, the Texaco gasifier[12] operates between 30 to 40 atmospheres and 1093^0 to 1538^{0}C, with a H_2/CO ratio of 0.8.

B. Explore methods for developing a form of thoria having both high
surface areas and good structural integrity. There are two standard
methods for approaching this problem. The first involves the manufac-
ture of a high porosity foamed ceramic pellet similar to those involv-
ing Zircon,[14] and other materials.[15] Another alternative is to
follow the procedures for manufacturing supported catalysts for other
metals; i.e., impregnation of an appropriate support (SiO_2 or
Al_2O_3 for example) with an aqueous solution of thorium nitrate,
followed by firing in air at a temperature high enough to partially
sinter the ThO_2 produced.

C. Define and scope the experimental conditions necessary to use the
catalyst developed in a 6" reactor, including factors dealing with
health and safety issues. This pilot plant demonstration could
presumably be carried out in existing facilities accessible to DOE.

We propose to carry out the tasks described above in a three-
year period. An approximate schedule to implement these tasks is shown
in Table IV.

Table IV. Timetable for proposed work.

	6	12	18	24	30	36
Develop and test supported catalyst						
Design, fabricate and test 1" reactor						
1" reactor: parametric study						
Define and scope conditions for test in large reactor (~6 in dia.)						

Time in months

4. POSSIBLE ADVANTAGES OF THE PROCESS

The manufacture of synthetic fuels over a thorium dioxide based catalyst offers the following advantages:

1) Reduction of plant investment by about 5-10% by relaxing input stream sulfur removal requirements.[6a,b,c,d]

2) Possible 10% reduction of operating costs by eliminating the need to change the catalyst every 6 to 7 weeks as it is now required by SASOL's Fe_2O_3 based system.[5] Thoria does not undergo losses in catalytic activity since it does not react with sulfur.

3) Easy coke removal, without sintering the catalyst, by passing air stream through the reactor when necessary.[2]

4) Use of a 1:1 H_2/CO mixture versus 3:1 or 4:1 now in use with iron based catalysts, thus eliminating required additional conventional process units.

5. POSSIBLE DISADVANTAGES OF THE PROCESS

Large scale implementation of a reaction scheme based on thoria will require the observance of careful monitoring and handling of the catalyst to meet the stringent requirements for maximum permissible ThO_2 concentrations in air and water. Dispersal of ThO_2 dust from a catalytic reactor can be kept to a minimum by utilization of high surface area ceramic foams manufactured from ThO_2 itself, or by its incorporation into a ceramic substrate. The use of high efficiency filters in the gas streams will also prevent the dissemination of ThO_2 powder. For additional details on this issue see the Appendix.

5. ESTIMATED ANNUAL MANPOWER AND OPERATING REQUIREMENTS

Chemist (Principal Investigator)	1.0 FTE
Chemical Engineer	0.25 FTE
Mechanical Engineer	0.25 FTE
Chemistry Technician	1.0 FTE
Electronic Support	0.5 FTE
Health Physicist	0.25 FTE
Other Support	0.25 FTE

$300K

Other Operating Expenses $ 50K (construction
                                cost of 1" reactor)   ⎤ one
                                                       ⎥ time
Equipment $ 50K (gas chromatograph   ⎥ cost
                                and control equipment) ⎦

TOTAL $400K

APPENDIX

IMPLICATIONS OF THE USE OF RADIOACTIVE ThO_2 AS A CATALYST

Thorium is a radionuclide with an exceptionally long half-life ($T_{\frac{1}{2}}$ = 1.39 x 10^{10} years) that decays mainly by α-particle emission. The decay scheme of Th^{232} is presented in Table V, where the daughters in equilibrium with thorium are identified along with their half lives, energies of radiation produced, percentage of disintegrations of the nuclide itself, quantity in grams per gram in equilibrium with Th^{232}, and the activity in curies per ton of thorium. In Equilibrium mixtures the total activity per ton of thorium is 1.063 curies or 0.934 curies/ton ThO_2.

From the viewpoint of radiation safety, the thorium catalyst itself poses no intrinsic radiation problem. All alpha and beta particles will be completely absorbed by the ThO_2, its ceramic support, and the walls of the reactor. Gamma rays should pose no problem either because the isotopes producing the most energetic gammas are present in relatively low concentrations (see Table V). For example, $_{81}Tl^{208}$ emits a 2.614 MeV gamma (100%) but the total activity in equilibrium is 0.038 curies/ton which can be reduced to negligible exposure levels by attenuation with ThO_2, the catalyst support, and the reactor walls.

Activation of C and H by gamma and alpha radiation via (α, n) and (γ, n) reactions is not thermodynamically possible, therefore there is no concern with producing activated radioactive hydrocarbons.

The maximum permissible concentrations allowable for ThO_2 in air and water for continuous exposure, as well as the maximum permissible body burden, are shown in Table VI. We are of the opinion that current technology can cope with the handling and containment of ThO_2 when used as a supported catalyst, thus meeting all safety regulations and standards without excessive additional costs. This factor will be considered in more detail during this study, but its demonstration will most likely have to wait until the pilot plant phase because of the low levels of radioactivity involved.

Table V. Decay scheme of $_{90}Th^{232}$.

Name	Symbols	Half life	Energy of Radiation (MeV) and Intensities*			Daughter per g Th, g**	Curies/ton Th
			α	β	γ		
Thorium	$_{90}Th^{232}$	1.39×10^{10} yr	3.95 (24%) 4.01 (76%)			1.0	0.100
Mesothorium 1	$_{88}Ra^{228}(MsTh_1)$	6.7 yr		0.055 (100%)		4.81×10^{-10}	0.102
Mesothorium 2	$_{89}Ac^{228}(MsTh_2)$	6.13 hr		1.18 (35%) 1.75 (12%) 2.09 (12%)	0.34 (15%) 0.908 (25%) 0.96 (20%)	5.05×10^{-14}	0.102
Radiothorium	$_{90}Th^{228}(RdTh)$	1.90 yr	5.34 (28%) 5.43 (71%)		0.084 (1.6%) 0.214 (0.3%)	1.37×10^{-10}	0.103
Thorium X	$_{88}Ra^{224}(ThX)$	3.64 days	5.45 (6%) 5.68 (94%)		0.241 (3.7%)	7.17×10^{-13}	0.104
Thoron***	$_{86}Rn^{220}(Tn)$	54.5 sec	6.29 (100%)		0.55 (0.07%)	1.24×10^{-16}	0.106
Thorium A	$_{84}Po^{216}(ThA)$	0.158 sec	6.78 (100%)			3.61×10^{-19}	0.114
Thorium B	$_{82}Pb^{212}(ThB)$	10.6 hr		0.346 (81%) 0.586 (14%)	0.239 (47%) 0.300 (3.2%)	8.72×10^{-14}	0.111
Thorium C	$_{83}Bi^{212}(ThC)$	60.6 min	6.05 (25%) 6.09 (10%)	1.55 (5%) 2.26 (55%)	0.040 (2%) 0.727 (7%) 1.620 (1.8%)	8.29×10^{-15}	0.110
Thorium C'	$_{84}Po^{212}(ThC')$	3×10^{-7} sec	8.78 (100%)			4.51×10^{-25}	0.073
Thorium C''	$_{81}Tl^{208}(ThC'')$	3.1 min		1.28 (25%) 1.52 (21%) 1.80 (50%)	0.511 (23%) 0.583 (86%) 0.860 (12%) 2.614 (100%)	1.43×10^{-16}	0.038
Thorium D	$_{82}Pb^{208}(ThD)$	Stable					

Total = 1.063

For footnotes see next page.

Footnote references for Table V.[+]

* Intensities refer to percentage of disintegrations of the nuclide itself, not to original parent of series.

** Radioactive equilibrium conditions.

*** For thorium used at a high temperature, some Rn^{220} should be volatilized as it is formed from Ra^{224} and its decay chain products (i.e., Po^{216}, Pb^{212}, etc.) should thus appear in the effluent stream or on the down stream filters rather than remaining in the catalyst bed.

+ Data taken from C. M. Lederer and Y.S. Shirley, eds, TABLE OF ISOTOPES (7th ed.; New York: Interscience 1978) and O. H. Hopgan, P. E. Zegman, and J. L. Mackin, BETA SPECTRA (USNDRL-TR-802) Washington, D.C., U.S. Atomic Energy Commission, 1964.

Table VI. Health physics for Th^{232} (ref. 17)

Maximum permissible concentration of natural Th (MPC) in air

$$= 1.8 \times 10^{-5} \text{ g/m}^3.$$

Maximum permissible concentration of natural Th in water

$$= 180 \text{ g/m}^3$$

Natural Th maximum permissible body burden = 0.01 μCi

or ~ 0.1 g

Critical organ = bone

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