1. SUMMARY AND RECOMMENDATIONS

1.1 SLURRY REACTOR

The slurry-phase bubble-column reactor is under development as an attractive alternative to the commercial Fischer-Tropsch (F-T) reactors. The main attractions of the slurry reactor are good temperature control and the ability to handle syngas of low H_2/CO ratio. Both of these improvements are attributable to the unique hydrodynamics of the slurry system.

Recommended work: Establishing reactor scale-up and design rules is the main thrust of current research. To this end, a better understanding of flow regimes with respect to such variables as liquid height, liquid properties, catalyst particle properties, and gas sparging is needed. There is still considerable disagreement concerning the interpretation of data on the degree of reactor mixing by means of mathematical modeling. Incorporation of the proper contributions from axial dispersion data may resolve this problem. To test this requires the knowledge of reliable correlations for the dispersion coefficients. Reliable correlations are also needed for such design parameters as gas holdup, mass transfer coefficients, diffusivity, and solubility. As far as the dimension of the experimental apparatus, those units currently in service among the DOE contractors should be adequate. Ranges of test conditions should be broad enough to cover all possible F-T reaction conditions.

1.2 CATALYTIC FUNCTIONS

In addition to the basic requirement of polymerizing CO/H_2, the ultimate slurry F-T catalyst would posess capabilities for:

- In-situ CO-shift

- High CO conversion per pass

- Selectivities for motor fuels beyond the Schulz-Flory limitations.

Substantial economic gains are anticipated from these additional capabilities. Thus they are the targets of many of the current research efforts, including those of DOE.

Some progress has been made, although details are often unavailable for proprietary reasons. Sections 3, 4, and 8 provide coverage of the progress. As a whole, catalyst development faces tough challenges. Imparting the multi-functions cited above to a single catalyst is a formidable challenge. The requirement that this catalyst maintain high activity in slurry phase makes the task doubly challenging. In this light, it is recommended that the development effort be structured in terms of several milestones which would eventually lead to the ultimate catalyst. Each milestone should be accompanied by an account of its economic impact.

A new class of methanol synthesis catalysts is emerging. These use palladium on various supports. This type of catalyst has not been used commercially, but it is of scientific interest because of the pronounced metal-support interactions that have been observed. It has been shown that some of the catalysts are at least as active as the conventional zinc-copper catalysts, and in some cases more active. In spite of considerable investigations, the reasons for the specific activity of supported palladium catalysts for methanol are not clearly understood. There is also no information regarding the effects of CO_2 and H_2O, which are common impurities in methanol synthesis, nor regarding activity maintenance, nor the feasibility of regeneration of spent catalyst.

The oxo reaction was discovered during the investigation of F-T reactions. After the discovery that the active catalytic species were homogeneous, the oxo development followed an independent path from that of F-T. Recently, however, the two technologies are coming within view of each other. Particularly, the slurry phase F-T is in a position to benefit from the know-how of the oxo technology, for example, regarding the reactor design including heat removal,

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product separation, etc. Heterogenization of the oxo catalysts has been tried with moderate success. The advantages of such catalysts are to gain heterogeneity for better product separation while retaining the inherent high activity and selectivity of the homogeneous catalyst. Between the extension of the F-T research toward adopting homogeneous catalysis and the interest in heterogenization of the oxo catalyst, there should be a fertile area where both F-T and oxo research can share their knowledge base.

1.3 ECONOMICS OF ADVANCED TECHNOLOGIES

The gasoline selling price for three synfuel cases estimated by Mitre (Section 5.4) are given in Table 1-1 in $/gallon and percent relative to a base case (Lurgi). In the mixed-output mode, replacing the Lurgi gasifier with BGC gasifier reduces the cost by 31%. A further reduction of 6% is achieved by replacing the Synthol with the Kolbel process. This relatively minor contribution by the Kolbel technology is rather surprising. The main reason is in the pricing of SNG, which Mitre has set at $6.17 per million Btu. Where methane can be sold at this price, converting it to gasoline and fuel oils apparently does not offer a significant incentive. The situation is different in the all-liquid mode, where methane is given zero value and is recycled to extinction via auto thermal reforming. Here, the Kolbel technology contribution is equal to that of BGC gasifier.

Although considerably improved over its predecessor, the Lurgi gasifier, the BGC gasifier still has deficiencies such as slow gasification rate, inability to handle caking coals and coal fines, and production of tars and large amounts of methane. The Texaco and Shell-Koppers gasifiers do not have these deficiencies and are therefore better suited for synfuel integration. Mitre evaluated these two gasifiers in the same economic framework and arrived at the following results. The values are only for the all-liquid mode, and the percentages are again relative to the base case (Lurgi).

The Shell-Koppers gasifier uses a dry-coal feeding and is more energy-efficient than the Texaco unit which is based on water-coal slurry feeding. This is

Table 1-1

Required Gasoline Selling Price
(1977 $)

Gasifier/F-T:	Lurgi/Synthol	BGC/Synthol	BGC/Kolbel
Mixed-output mode			
$/gal	1.33	0.92	0.84
%	100	69	63
All-liquid mode			
$/gal	1.51	1.24	1.03
%	100	82	68

"Mixed:" Methane from gasifier and F-T is sold as SNG at $6.17/mmBtu
"All-liquid:" Methane is reformed and recycled to F-T.

reflected in the synfuel economics. The cost reduction from the base case is 23% when the Shell-Koppers unit is substituted for the Lurgi unit, compared with 19% for the Texaco gasifier. Replacing the Synthol with the Kolbel process reduces the cost by 14% when the gasifier is a Texaco unit, and 15% with the Shell-Kopper unit.

In summary, approximately equal economic incentives exist for the advanced gasifier and for the slurry F-T process. The noteworthy item of the Mitre study is the impact of the advanced gasifier, indicating that a synfuel plant of improved economics is as near as development of the improved gasification technology. Some additional improvement is expected from a Kolbel-type technology, but its prospect is believed not as near-term as the advanced gasifiers.

The ability of the slurry phase F-T to accept syngas of low H_2/CO ratio is well suited for integration with advanced coal gasifiers that characteristically produce low H_2/CO syngas. The elimination or reduction of CO-shift, which would otherwise be required with the Synthol process, results in some cost savings. It is estimated that the savings relative to an advanced gasifier-Synthol combination are less than 5% in terms of total capital and less than 1% in production cost.

1.4 SOLVENT EFFECTS IN SLURRY REACTIONS

The liquid medium for the slurry process is a complex mixture, and its composition may change with time. The question of how this change may affect the catalyst performance or the process operability as a whole has not received much attention. It is recommended that the subject of solvent and its relationship to slurry-phase catalysis be explored.

In similar reaction systems, research in solvent effect has proven fruitful. For example: in direct coal liquefaction, the discovery of donor solvent has had important impacts on process development. Also, evidence is emerging that small concentrations of selected solvent components could reduce the liquefaction

Table 1-2

Required Gasoline Selling Price, All-liquid Mode
(1977 $)

	Lurgi/Synthol	BGC/Synthol	BGC/Kolbel
$/gal	1.51	1.24	1.03
%	100	82	68

	Lurgi/Synthol	Texaco/Synthol	Texaco/Kolbel
$/gal	1.51	1.23	1.01
%	100	81	67

	Lurgi/Synthol	Shell-Koppers/Synthol	Shell-Koppers/Synthol
$/gal	1.51	1.16	0.94
%	100	77	62

severity. This development is somewhat similar to liquid-phase homogeneous catalysis, where trace amounts of promotor could greatly enhance the catalyst activity (Section 3.4).

1.5 ANALYTICAL CONTRIBUTIONS

The slurry catalyst research at Union Carbide (sponsored by DOE) has a subcontract with the University of California at Berkeley. In this arrangement, the Berkeley group, led by Professor G. Somorjai, is to investigate various fundamental aspects of Fischer-Tropsch catalysts using modern ultrahigh vacuum techniques. This type of arrangement is often found in large research contracts. Success is largely dependent on both the level of expertise of the subcontractor and task coordination. The latter is particularly important to maintain a perspective of relevancy and to promote synergism between the work being performed by both parties. In these regards, the arrangement between the Berkeley group and Union Carbide appears to be successful.

The Berkeley group is using a mass spectrometer for thermal desorption spectrometry, low-energy diffraction for surface structure, Auger electron spectroscopy for determining the atomic composition of the catalyst surface, and x-ray photoelectron spectroscopy to obtain information on the oxidation state of major surface components. All of these vacuum analytical features are housed within a single vacuum chamber for simultaneous examination of a given surface condition of a catalyst sample.

A multifunctional analytical instrument such as the one used by the Berkeley group is a powerful research tool. Instruments having various vacuum techniques are being used. Considerable expertise is required to operate the instruments and interpret the results, and it is quite expensive.

The high vaccuum requirement of these modern analytical techniques is a deterrent to in-situ investigation of catalytic surfaces under reaction conditions. Some researchers have overcome this limitation by modifying hardware. An example is controlled atmosphere electron microscopy (CAEM), advanced by R.T.K. Baker of

Exxon. This system employs a transmission electron microscopy of ~3nm resolution, allowing observation of catalysts in action, under pressures of up to a few pounds per square inch and at any desired temperature (Section 7.4).

A semi-in-situ capability is also achieved by the experimental set-up of the Berkeley group mentioned above. In this system, a catalyst sample can be subjected (if desired) to reaction conditions up to 1-20 atm pressure and at any desired temperature. This is accomplished by means of a small sample space mechanically created inside a high vacuum bell-jar. Upon the completion of reaction, the catalyst is exposed to a vacuum and is then ready for surface analysis (Section 7.2).

1.6 STRONG METAL-SUPPORT INTERACTIONS

Metal-support interactions in catalysis have long been recognized, but closer examination is just beginning (Section 6). Discussion of the topic is becoming increasingly common and significant advances are being made thanks to advances in analytical techniques. Recent evidence suggests that metal-support interactions are widespread phenomena of differing strength, which is influenced by three key properties of matter in interaction:

- Energetics of metal particles: properties reflecting the cohesive energy of a particle

- Geometric properties: those describing the shape, size, crystal habit, order, strain, and structure

- Electronic properties: those describing the band structure, electron binding energies, and interactions of electrons with magnetic fields.

Some authors feel it necessary to clarify the interactions into weak, medium, and strong categories. The allocation of various interactions to each category is somewhat arbitrary at this time, but it is generally accepted that metals on oxides such as SiO_2, and Al_2O_3, and MgO, and carbon or graphite show weak

interactions (exceptions may exist when the oxide support is subjected to very high reduction temperature); highly dispersed metal on zeolite shows medium interactions; and metals on reducible oxides, especially TiO_2, show strong interactions.

Strong metal-support interactions (SMSI) have been observed with dispersion of most of the Group VIII metals: platinum, iridium, osmium, palladium, rhodium, and ruthenium on TiO_2. When these catalysts are reduced above a certain temperature, SMSI is induced and increases with temperature. H_2 and CO chemisorption are widely used as a means of detecting SMSI. A candidate catalyst reduced below a critical temperature will show a normal chemisorption capacity for H_2 or CO, but when the reduction temperature exceeds the critical level, SMSI will reduce the chemisorption capacity. This is demonstrated with the Group VIII metals on TiO_2, as shown in Tables 1-3 and 1-4 (35).

Metal-support interaction varies with reduction temperature and among different oxide supports (Section 6.2). The work of Tauster and Fung (41) illustrates these effects as plotted in Figure 1-1. Temperature is clearly a major factor. There are two distinct groups of oxides: one group shows little change and the other group, including Ta_2O_5, V_2O_3, TiO_2, MnO, and Nb_2O_5, shows marked changes. The latter SMSI appears to be a reversible process. In other words, SMSI induced by high temperature reduction can be removed by oxidation. Steam may be used in place of oxygen (Section 6.4).

Electron microscopic observations show that metal particles under SMSI have a flat, "pill-box" outline, instead of the usual hemispherical shape. It is speculated that under SMSI, the oxide support becomes more "wettable" by metal. This causes metal to spread thinly.

Investigation in metal-support interactions is progressing. The observations made thus far reinforce the view that metal-support interaction plays some important roles in catalysis. Clearly, SMSI in F-T synthesis is a relevant research topic with potential benefits.

Table 1-3

Hydrogen Chemisorption on TiO$_2$-supported Group VIII Noble Metals

| Metal (2 percent by weight)	Ratio of hydrogen atoms adsorbed to total metal atoms	
	Reduction at 200°C	Reduction at 500°C
Ruthenium	0.23	0.06
Rhodium	0.71	0.01
Palladium	0.93	0.05
Osmium	0.21	0.11
Iridium	1.60	0.00
Platinum	0.88	0.00

Table 1-4

Carbon Monoxide Chemisorption on TiO$_2$-supported Group VIII Noble Metals

Metal (2 percent by weight)	Ratio of carbon monoxide molecules adsorbed to total metal atoms	
	Reduction at 200°C	Reduction at 500°C
Ruthenium	0.64	0.11
Rhodium	1.15	0.02
Palladium	0.53	0.02
Iridium	1.19	0.00
Platinum	0.65	0.03

Note that reduction at 500°C reduces or completely eliminates the chemisorption capacities of these catalysts.
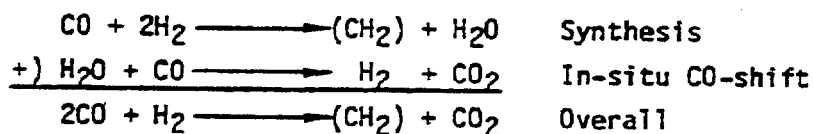
H Atoms per Atom
of Total Metal
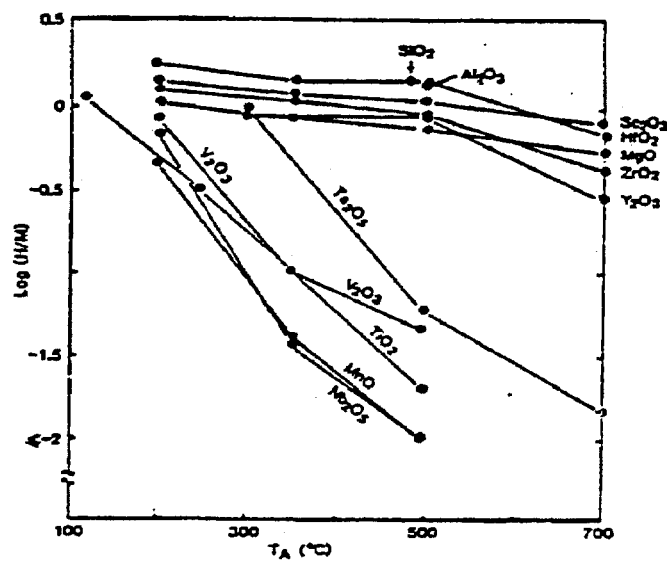
Reduction Temperature
(1 hr under flowing H₂)

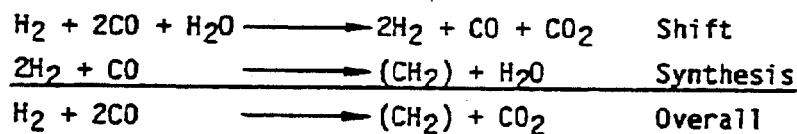Figure 1-1. Hydrogen Chemisorption on Ir on Various Supports

1.7 CO_2 AS A BY-PRODUCT OF SLURRY REACTION

The absence of a required external CO-shift is an accepted advantage of slurry reactors over the gas-phase F-T reactors. Another advantage, not often cited, is the fact that CO_2 is the by-product of synthesis reactions, not H_2O as in the gas-phase reactor. The overall reaction is:

$$CO + 2H_2 \longrightarrow (CH_2) + H_2O \quad \text{Synthesis}$$
$$+) \; H_2O + CO \longrightarrow H_2 + CO_2 \quad \text{In-situ CO-shift}$$
$$\overline{2CO + H_2 \longrightarrow (CH_2) + CO_2} \quad \text{Overall}$$

Under this idealized condition, a syngas of 0.5 H_2/CO will yield only CO_2 as the by-product. Since CO_2 is a gas, it is easy to separate out from the F-T products, whereas extensive waste treatment would be necessary for the liquid by-product of gas-phase synthesis.

The process implication of this CO_2 by-product can be reviewed from the standpoint of overall F-T plant operation. For a raw syngas having, for example, a H_2/CO = 0.5 mol/mol from an advanced gasifier, the integration with the Synthol unit requires CO shift. After CO_2 removal, the shifted syngas is synthesized. The overall reaction is:

$$H_2 + 2CO + H_2O \longrightarrow 2H_2 + CO + CO_2 \quad \text{Shift}$$
$$\underline{2H_2 + CO \longrightarrow (CH_2) + H_2O} \quad \text{Synthesis}$$
$$H_2 + 2CO \longrightarrow (CH_2) + CO_2 \quad \text{Overall}$$

Note that the overall reaction is identical with that for the slurry F-T process. This implies that both require removal of an equal amount of CO_2, differing only in whether it is done before or after the F-T step.

1.8 THE SCHULZ-FLORY MECHANISM

Fischer-Tropsch synthesis over conventional iron catalysts has been documented to show that the hydrocarbon formation follows a random polymerization mechanism known as a Schulz-Flory (S-F) mechanism.

A striking fact about the S-F product distribution is the sharp drop in the weight percent of the most abundant components as the degree of polymerization increases. Economic factors operating in today's market dictate preference toward more selective product distribution over that of S-F. This is the driving force behind a number of research activities to "bypass" S-F.

Two basic approaches to bypassing S-F are:

- One-step approach (Union Carbide)

- Two-step approach (Mobil methanol-to-gasoline).

The development of Mobil's ZSM-5 catalyst has advanced the Mobil MTG process to the forefront of the S-F bypass efforts.

Union Carbide and Air Products are funded by DOE to develop the one-step catalyst operative in slurry phase. This catalyst must possess the following basic capabilities:

- CO shift

- Polymerization

- Selective termination of polymerization

- Operation under slurry environment

- High CO conversion per pass.

Both efforts are in the early stage and catalyst compositions are held as proprietary. Preliminary results show that the proprietary catalysts are indeed able to make more motor-fuel range products than what is predicted by the S-F distribution. Considerable improvements are needed in selectivity and CO conversion per pass. Development work addressing activity maintenance and perhaps spent catalyst regeneration are yet to be started.