



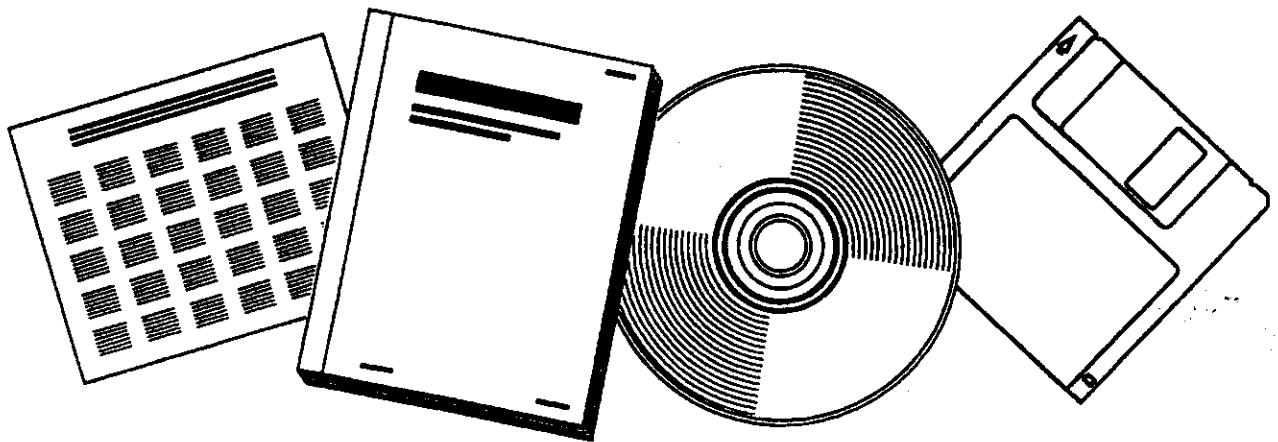
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SYNTHESIS GAS CONVERSION IN A MIXED SLURRY REACTOR WITH IRON-MANGANESE CATALYSTS

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SYNTHESIS GAS CONVERSION IN A MIXED SLURRY REACTOR WITH
IRON-MANGANESE CATALYSTS

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ABSTRACT

Synthesis gas was reacted over different compositions of iron-manganese Fischer-Tropsch catalysts in a slurry reactor. The reactor operates in a back-mixed mode with a continuous flow of feed gas through the catalyst suspended in the liquid medium. Four catalysts with iron-manganese ratios of 57/43, 44/56, 22/78, and 10/90 were investigated at identical process conditions after a standard activation procedure. With time on stream for each catalyst system, hydrogenation of olefins occurred, along with olefin isomerization reactions. Activity, selectivity, and stability are discussed in general. Analyses of used catalyst samples are also reported.

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INTRODUCTION

With the renewed interest in synthetic fuels from coal during the late 1970's, several aspects of indirect liquefaction research have been explored. Two areas of much investigation are reactor design and catalyst design. In particular, the slurry bubble column reactor has recently been given considerable attention (1). Major advantages of such a system are the excellent temperature control, the high conversion per pass, and the ability to process the low hydrogen to carbon monoxide ratio synthesis gas characteristic of second generation gasifiers (2).

Investigative results with a specific catalyst system, iron-manganese oxide, can be described as being very interesting but scattered. In past Fischer-Tropsch work, small amounts of manganese were used to promote iron catalyst, resulting in an increased activity to convert hydrogen and carbon monoxide mixtures (synthesis gas) to longer-chain hydrocarbon products (3). German researchers (4), with the goal of producing light α -olefins for manufacture of petrochemicals, claimed in the patent literature that gas phase synthesis reaction with a coprecipitated iron-manganese catalyst would yield a product that is predominantly C_2-C_4 light olefins, has a chain length extending only to about C_6 , and has a trace amount of methane. Specific catalyst compositions, with a maximum iron content of 50 Fe/50 Mn, were used, along with a specific activation and startup procedure. Later work by these investigators (5) with a low Fe/Mn ratio catalyst indicated that some C_5^+ material was formed in the gas phase reaction, but in contrast to the gas phase reaction, a much lower light olefin selectivity occurred, along with a greater C_5^+ selectivity in the slurry reaction.

Schulz and workers (6) investigated various promoted coprecipitated iron-manganese catalysts in a gas phase system. Results indicate with increasing manganese content of the "matrix" catalyst, secondary olefin hydrogenation, which parallels olefin isomerization reactions; is suppressed. In all these tests, a potassium promoter was added to the matrix catalyst, and it was reported that the alkali content of the catalyst reduces the degree of secondary olefin double-bond isomerization.

Other investigators have reported interesting gas phase screening results with various iron-manganese compositions. Van Dijk and colleagues (7) found that Fischer-Tropsch synthesis at 240°C on several coprecipitated catalysts with differing manganese contents, prepared by batch precipitation techniques, showed no relation between the olefin selectivity of the catalyst and the amount of manganese added. Furthermore, the fully carburized iron-manganese oxide catalyst revealed a Schulz-Flory distribution that was quite similar to that of a carburized iron catalyst without manganese oxide. On the other hand, Barrault and workers (8) investigated the Fischer-Tropsch synthesis with a batch coprecipitated iron-manganese catalyst on an alumina support. After a hydrogen reduction, a maximum in light olefin selectivity was obtained for a Fe/Mn=1 bulk composition. In a later communication (9) by these same researchers, hydrocarbon synthesis with a manganese oxide support that was impregnated with a small loading of iron produced a highly olefinic light gas yield with a suppression of methane. When this manganese oxide was used as the support, the chemisorptive properties of the catalyst were affected, suggesting a type of strong metal support interaction effect. Diefenbach and workers (10) investigated a 10 Fe/90 Mn catalyst, along with other iron-based catalysts, in gas phase

microreactor screenings. Results indicate the iron-manganese catalyst had the highest light gas olefin content in the study, and the methane formation was suppressed. Similarly, Lehmann and investigators (11) tried to optimize an iron-manganese catalyst that was formed in a continuous precipitation unit. Their findings in fixed-bed tests indicated that up to 47 percent of the hydrocarbon product could be C₂-C₄ hydrocarbons, with 84 percent of this fraction being olefinic. Also interesting is the fact that the methane formation was suppressed, since only 70 percent of the theoretical amount of methane predicted by Schulz-Flory was formed.

Investigators have also studied the iron-manganese system in the slurry phase. Deckwer and coworkers (12) investigated a low ratio Fe/Mn catalyst in a bubble column reactor. The catalyst was precipitated in a continuous flow unit and activated in situ by following a procedure of Kölbel (4). Although there is some question about deactivation during the tests (13), the syngas conversion revealed a product distribution that followed conventional Schulz-Flory kinetics. The higher yields of C₂-C₄ hydrocarbons with these type catalysts was explained as being due to the lower value of the chain growth probability. Operation in both a gas phase fixed bed and a slurry phase yielded the same product slate for the iron-manganese catalyst, implying that the chain growth probability does not depend on the type of operation. In a limited study, Satterfield (13) also investigated a low ratio Fe/Mn catalyst in a stirred autoclave slurry reactor. Although catalyst activation was similar to that described by Kölbel, Satterfield concluded that secondary hydrogenation and olefin isomerization reactions appear to be significant with the Fe/Mn catalyst. Hydrocarbon products below C₁₀ followed a typical Schulz-Flory distribution.

The present work is part of a larger indirect liquefaction research program to investigate catalyst systems that can process low ratios (0.5/1 to 1/1 of H₂/CO) of synthesis gas to produce a high yield of light olefins and gasoline-range hydrocarbons. Low-ratio synthesis gas will be efficiently produced from second-generation gasifiers (2). To eliminate a costly external shift process, which most gas-solid phase Fischer-Tropsch catalytic reactors require, the low-ratio synthesis gas can be reacted in a slurry reactor.

One process concept for producing gasoline from synthesis gas is the two-stage method (14). A slurry reactor with iron-manganese catalyst is a potential candidate for the first stage, since a light olefinic product, as reported, can be formed and sent to the second stage to react over ZSM-5 or a modified zeolite to yield a high-octane gasoline fraction. Interesting initial results with iron-manganese catalysts warranted further testing of this catalyst system. By investigating various compositions of the iron-manganese catalyst, the catalyst activity and selectivity to olefins were determined as a function of both the catalyst composition and the catalysts' general behavior in the slurry phase.

EXPERIMENTAL

The catalyst batches were prepared in a continuous precipitation reactor with built-in stirrer blades similar to the unit used by Kölbel and co-workers (15). The precipitator has an internal volume of 0.180 liter. Sufficient reagent-grade Fe(NO₃)₃ · 9H₂O and Mn(NO₃)₂ to produce 140 grams of FeOOH + Mn(OH)₂ precipitate were diluted with deionized water to yield

2.0 liters of solution. An amount of reagent-grade ammonium hydroxide equal to 2.4 times the stoichiometric amount for complete precipitation was diluted with deionized water to yield 2.5 liters of solution. These two feed solutions were heated in stainless steel beakers to 85°-90°C before being mixed in the precipitator. The exact concentrations used in each run are given in Table 1. In several preliminary runs, the salt and ammonia feed batches were diluted to 3.0 liters and 3.5 liters, respectively. However, increasing the concentration did not affect the pH in the precipitator and greatly reduced the amount of precipitated slurry that needed to be filtered. Therefore, all following runs were made with the more concentrated solutions.

The precipitator was preheated and maintained at 90°C by means of a circulating constant-temperature bath. The internal stirrer was maintained at 950 rpm. The ammonia feed was started approximately 15 seconds before the metal feed to increase the pH in the reactor before the metal introduction. Both pumps were maintained at a flow rate of 0.19 L/min. Although the pH was measured at the exit of the reactor, no attempt was made to control it by varying the feed rates, since little variation in pH occurred during a run. Catalyst batch reproducibility could be obtained by maintaining the feed concentrations and feed rate constant.

The slurry from the precipitator was collected on a 24-inch Buchner filter. Filtration was rapid at the beginning of the run but slowed considerably during the second half of the run, allowing slurry to collect in the filter funnel. Depending on the amount of iron in the precipitate, approximately 15-30 minutes were required to complete the filtration after completion of

Table 1. Preparation Characteristics of Iron-Manganese Catalysts

Test	Target Fe/Mn Ratio	Metals Conc. (g metal/liter)	NH ₃ Conc. (f)	pH filtrate	% Fe (wt%)	% Mn (wt%)	% Fe (Metal Basis)
SL-45	10/90	43.3	5.30	9.5	6.4	60.1	9.6
SL-43	20/80	49.6	6.72	9.2	15.0	53.8	21.8
SL-42	35/65	46.6	7.15	8.7	28.2	35.5	44.3
SL-40	50/50	46.6	7.15	9.1	36.1	27.5	56.8

the precipitation. A sample of the filtrate was collected for pH measurement, then the filter cake was washed with two liters of hot water. The washing step is quite slow.

The filter cake was transferred to a vacuum oven and dried under 30 inches of vacuum at 140°C overnight. Because the preliminary washing step is slow and probably not complete due to occluded and adsorbed ions, the dried cake was broken up into small pieces and placed in one liter of hot water and allowed to sit for 1-2 hours. The material was then refiltered and washed with an additional liter of hot water. The filter cake was redried under vacuum at 140°C for four hours. The catalyst was then crushed and sieved through 325 mesh (44 μm).

The studies were conducted in a one-liter stainless steel stirred reactor as described by Zarochak and workers (17). A schematic of the reactor system is seen in Figure 1. Synthesis gas is stored in large gas holders at ambient conditions. The gas is then boosted to high pressures after going through a silica gel trap for dehumidification and an activated-carbon trap to remove sulfur impurities. To prevent carbonyl formation, the high-pressure gas is stored in a bank of aluminum cylinders rather than carbon steel cylinders. Before entering the system, the gas again flows through an activated-carbon trap. The flow is metered and controlled by a mass flowmeter, and other gases can be blended with the 1H₂/1CO synthesis gas via a similar apparatus. Products and unreacted synthesis gas exit the reactor overhead via a coiled reflux condenser with a 200°C exit temperature. This stream then enters a hot trap (200°C), where heavy hydrocarbons, if produced, are condensed. Light products are condensed in a series of

water-cooled traps. The product gas is metered by a wet test meter and can be directed to an on-line gas chromatograph that can analyze hydrocarbons up to C₃ and separate isomers up to C₄.

The iron-manganese catalysts in all the tests were activated in an identical manner: an in situ carbon monoxide activation followed by synthesis conditions. Various activations with a 10 Fe:90 Mn catalyst in a gas-phase microreactor were investigated by Diffenbach (18), who concluded that the manner in which the catalyst is brought on stream after the activation procedure is as important as the activation procedure itself. The activation procedure in this investigation was similar to that reported by Diffenbach.

Fifty grams of iron-manganese catalyst that were sieved through 325 mesh (44 μ m) were placed in the reactor with the molten medium wax to make a 13.5 weight percent suspension based on unreduced catalyst weight. The high-boiling paraffinic wax was designated P-22 from Fisher Scientific Company and has an average carbon number of 28. The reactor system was sealed, cooled, leak-tested, and purged with helium. At 200 psig system pressure, the temperature was increased to 275°C under a flow of helium. By means of a sliding thermocouple in a thermowell in the reactor, isothermal conditions within the reactor were established. The impellor was stopped and gas flow was decreased to a small amount, at which time the unexpanded slurry level was lowered to 0.5 liter by using the reactor pressure to force the excess wax through a dipleg and filter and into a heated-wax trap. After this, the impellor was restarted, and once isothermal and isobaric conditions were reestablished, the inert flow was stopped and carbon

monoxide was introduced. Activation with carbon monoxide lasted for twenty-four hours at 275°C, 200 psig, and a WHSV of 2.25 hr⁻¹, during which time the concentration of carbon dioxide in the exit gas approached a constant value. (WHSV is defined as grams of gas per hour per gram of unreduced catalyst.) At the end of this activation, the liquid level was again readjusted and the system pressure maintained at 200 psig with carbon monoxide. Synthesis gas was introduced in increments over the next hour until the desired space velocity for the test was reached. Trap drainings, flows, and gas analyses were measured on a twenty-four hour basis for material balance determinations. Unless otherwise stated, tests in this study used a 1H₂:1CO feed gas.

The gaseous and liquid products were characterized by various analytical techniques. Gas exiting the reactor system was analyzed for hydrogen, carbon monoxide, carbon dioxide, nitrogen, and hydrocarbons up to C₈ by gas chromatography. The liquid condensate in the trapping system was collected and physically separated into an aqueous fraction and an oil fraction. The aqueous phase was analyzed by mass spectroscopy to detect oxygenates, and the water content was determined by the Karl Fischer reagent technique. The liquid hydrocarbon samples were characterized by gas chromatographic simulated distillation ASTM D-2887 to determine boiling range distributions, by fluorescent indicator adsorption ASTM D-1319 to determine the functionality of the liquid oil, and by bromine number ASTM D-1159 to check the olefin content. Infrared studies were also performed on the oil fractions. Relative amounts of terminal, trans-internal, and beta-branched-terminal olefins were determined by infrared spectral analysis. The wax fraction was dependent on the trapping system and was analyzed by gas chromatographic

simulated distillation and bromine number. Selected liquid oil and wax samples for a particular period of time were also analyzed by gas chromatography with a capillary column, as described elsewhere [16].

RESULTS AND DISCUSSION

Two of the first tests investigated were those for precipitated iron and precipitated manganese. The precipitated manganese was activated in the slurry by reducing the catalyst in situ with carbon monoxide followed by hydrogen, similar to the procedure proposed by Kolbel [4]. However, the activity and, thus, conversion of synthesis gas over the manganese were negligible.

The unpromoted precipitated iron was activated in situ with synthesis gas at 250°C and 200 psig for 24 hours. Although this activation procedure was not necessarily optimum, higher reduction temperatures were avoided to prevent possible sintering of the precipitate. The conversion at 275°C was low for this test, possibly indicating incomplete initial reduction, but the high methane content (14 weight percent) in the hydrocarbon product was indicative of an iron catalyst at elevated temperature. The olefin content in both the C₂-C₄ fraction and the liquid oil was less than the paraffinic content, which is expected since the catalyst was not promoted.

Four catalysts with iron-manganese weight ratios of 57/43, 44/56, 22/78, and 10/90 were individually investigated after the identical activation procedure and at identical initial process conditions of 275°C, 200 psig, and 1.21 WHSV of 1H₂/1CO synthesis gas. During several of the tests, the

impellor speed was varied to ensure that bulk mass and thermal transfer resistances were minimal in the slurry phase operations. Good reproducibility between tests with catalyst from the same batch was always achieved if identical activation procedures and process operations were followed.

Following introduction of synthesis gas to the reactor, catalyst activity did not stabilize until after a particular period. For the two lower compositions of iron, a steady conversion was obtained after 12 hours on stream, whereas for the two catalysts with higher iron loadings, the conversion did not level out until after 24 hours on stream. The catalyst activity plotted versus time did not go through a minimum and then continuously increase, as observed by Satterfield (13) with a 10 Fe/90 Mn catalyst, but rather increased to a maximum activity after 12 hours. Differences in these results could be explained by the activation step in general and by the actual procedure for introducing synthesis gas. Schulz and workers (6) indicate that a stationary state is obtained only after two days of operation with an iron-manganese matrix catalyst. They related this observation to the fact that iron catalysts undergo changes in oxide and carbide composition with time on stream. In this communication, comparisons between tests will be made after the initial 24-hour period.

Throughout all the tests, a similar deactivation trend was found with time on stream. As seen in Table 2 and Figure 2, the conversion decreased with time on stream, and the selectivity shifted to a lighter fraction. An example is test SL-43 in Table 2. The (H₂ + CO) conversion dropped from 38.7 at 45 hours to 31.9 after 165 hours on stream. The iron-manganese catalysts with the higher iron contents deactivated more rapidly over the

Table 2. Reaction Results with Iron-Manganese Catalysts at 1.21 MHSV, 275°C, and 200 psig

Test No. Fwd/Rev Ratio	40 57/43		42 41/56		43 22/78		45 10/90		47 Fused Iron			
	46	47	48	49	50	51	52	53	54	55		
Time On Stream, hr	166	40	120	160	117	165	261	45	125	45	117	175
CO-Conversion, mole percent	39.2	57.9	30.7	30.0	40.3	32.6	27.0	22.2	17.9	15.5	10.1	21.8
(H ₂ /CO) Conversion, mole percent	40.1	54.5	31.5	30.3	38.7	34.8	25.5	23.9	19.4	17.6	9.9	19.9
Hydrocarbon Distribution, wt percent												
C ₁ H ₄	8.4	11.0	9.2	12.3	6.2	6.7	8.9	7.2	8.8	10.5	9.3	4.7
C ₂ -C ₄	30.2	35.3	37.1	35.2	31.1	35.5	39.1	35.2	36.9	39.3	36.4	20.3
C ₅ ⁺	61.4	50.0	53.5	52.5	62.7	57.8	52.0	57.6	54.3	50.2	54.3	74.0
Olefin Content, C ₂ -C ₄ Fraction, wt percent	59.5	49.6	53.7	52.8	79.5	73.7	63.8	70.7	60.0	58.9	83.7	80.8
Internal/Terminal-Olefin Ratio of Oil Product	0.63	---	0.56	---	0.26	0.61	---	0.86	---	3.75	0.04	0.07
ols 2-Butene/1-Butene Ratio	0.26	0.37	0.21	0.33	0.08	0.15	0.19	0.27	0.18	0.44	0	0.06
Liquid Oil Product Composition, vol percent												
Olefins	64	60	54	67	72	66	62	73	63	53	77	83
Saturates	27	35	39	24	17	22	28	20	30	41	13	13
Aromatics/Oxygenates	8	5	7	0	11	11	9	7	7	6	10	8

a) 1.71 MHSV, 250°C, 200 psig.

first 100 hours than the lower iron-containing catalysts of tests SL-43 and SL-45 (see Figure 2).

As expected, the conversion is higher initially for the catalyst with the higher composition of iron, but the deactivation rate of these catalysts is also much greater than the deactivation rate of the catalysts with lower iron composition. Test SL-42 in Table 2 indicates a large decrease in (H₂ + CO) conversion over a 120-hour period. Possible explanations for this behavior could be that the catalyst was not entirely stabilized before the test was begun or that the higher amount of manganese aided in stabilization. Also, although each catalyst is activated in an identical manner, the optimum activation procedure may be different for each catalyst composition. Comparisons between tests were made after the same time on stream (approximately 45 hours).

The selectivity of the various iron-manganese catalysts also varies with time; the carbon number distribution shifts to a lighter fraction (see Table 2). For example, in test SL-43, the methane percent increases from a low of 6.2% after 45 hours to 7.7% after 165 hours on stream. With time on stream, the C₂ to C₄ fractions also increase, but the C₅⁺ fraction decreases.

The functionality of the product also changes with time on stream for all the iron-manganese catalysts investigated. The light olefin content decreases with synthesis time, possibly due to olefin hydrogenation. This is paralleled by FIA results on the liquid oil, which reveal that with time on stream the oil becomes more paraffinic and less olefinic. Also with

catalyst aging, the olefinic products exhibit more double-bond isomerization. If the cis 2-butene/1-butene ratio is used as an index for olefin isomerization, this ratio -- thus, isomerization -- increases in the C₄ fraction with time. Similarly, by infrared analysis of the liquid oils, the ratio of internal to terminal olefins increased with time during each catalyst test. Satterfield (13) also reports that secondary hydrogenation and olefin isomerization reactions appear to be significant with iron-manganese catalysts. Results from a fused-iron catalyst (an ammonia synthesis catalyst type C73-1-01 made by United Catalyst, Incorporated) are compared with those from the iron-manganese catalysts in Table 2. Virtually no change in olefinic content or olefinic isomers occurred with the fused-iron catalyst over the 175 hours on stream. Also, for the iron-manganese catalysts compared at similar times on stream, the olefinic fraction in the hydrocarbon product from the lower iron-containing catalysts is greater than that from the higher iron compositions, as shown by the olefinic content in the light gas and liquid oil.

Process parameters were investigated during these tests and others with the various iron-manganese compositions. The effects of temperature and space velocity on catalyst performance were investigated akin to Lehmann (11), who found that these two process variables influenced the C₂-C₄ olefin yield. Qualitative results shown in Table 3 indicate that with an increase in space velocity, the methane and C₂-C₄ selectivities increase very slightly, and the C₂-C₄ olefin yield increases, but the isomerization -- as denoted by the cis 2-butene/1-butene ratio -- decreases slightly. A temperature increase has the greatest effect by increasing methane and C₂-C₄ selectivities, decreasing the C₂-C₄ olefin yield, and increasing olefin isomerization.

Table 3. Effect of Process Parameters on Conversion and Hydrocarbon Selectivities

<u>Process Parameter</u>	<u>CO-Conversion</u>	<u>Methane Selectivity</u>	<u>C₂-C₄ Selectivity</u>	<u>C₂-C₄ Olefin Selectivity</u>	<u>C₂-C₄ Olefin Yield</u>	<u>Ratio cis 2-butene to 1-butene</u>
Space Velocity Increase (Range 0.60-2.41 WHSV)	Decrease	Slight Increase	Slight Increase	Increase	Increase	Slight Decrease
Temperature Increase (Range 250°-290°C)	Increase	Increase	Slight Increase	Decrease	Decrease	Increase

The reaction temperature for several of the iron-manganese catalysts was varied to determine temperature effects on kinetic factors. A model for this type of stirred-autoclave, semicontinuous flow unit was developed by Satterfield [19] with the assumptions that the rate of hydrogen and carbon monoxide consumption is first order with respect to the concentration of hydrogen and that diffusional effects are minimal. The overall activity constant was calculated at the same process conditions except for the temperature, which varied from 250°C to 290°C. Activation energies were obtained from Arrhenius plots.

<u>Catalyst</u>	<u>Activation Energy, kcal/mole</u>
57 Fe/43 Mn	17.3
22 Fe/78 Mn	19.3
10 Fe/90 Mn	18.3
Unpromoted Precipitated Fe	24.5
Fused Fe	25.3

The activation energies, which were obtained from the model for vapor-phase comparisons, are within the range of those reported for fixed-bed, vapor-phase studies over an iron catalyst (17-27 kcal/mole) [20]. Deckwer [12] reports an activation energy of 26 kcal/mole for results in a bubble column reactor with a continuous precipitated 10 Fe/90 Mn catalyst.

ANALYSES OF USED CATALYSTS

After each test, the catalyst in the reactor was recovered. Catalyst recoveries averaged about 94 percent. The slurry was hot-filtered to remove most of the catalyst, and the filtered catalyst was washed in a Soxhlet

extractor for 48 hours with hot toluene. The catalyst was then vacuum-dried at 110°C overnight. The samples were analyzed by bulk chemical methods, X-ray diffraction, BET surface area determination, and scanning electron microscope (SEM); results from these analyses are listed in Table 4.

Bulk chemical analysis reveals a higher concentration of carbon on all used catalysts as compared to the fresh catalysts. The highest temperature for all catalysts in Table 4 was 275°C except in test SL-45, which had a 1-day period at 290°C. The amount of carbon per gram of iron per hour on stream was greater for the catalysts with higher iron/manganese ratios. This can be related to Figure 2, for the catalysts with higher deactivation rates are those containing a high amount of iron. These results indicate that carbon formation or coking could be a cause for deactivation. X-ray diffraction results indicate an iron carbide phase for the higher iron-containing catalysts. Although carbide was not detected in the catalysts having smaller iron concentrations, this may be due to detection limitations in the X-ray analysis. A manganese carbonate phase is observed in the two catalysts that deactivated most rapidly.

The BET surface area results reveal a decrease in surface area of the used catalysts as compared to the fresh. On the other hand, the mean pore diameter increased with catalyst usage. Sintering of the fresh catalyst could explain this behavior. Similar results were obtained in gas phase screening tests. In contrast to this, the fused-iron catalyst, which had a small surface area, increased in surface area after usage. A large morphological difference between coprecipitating a catalyst and fusing one from a melt is apparent in the BET results of Table 4. An optical method

Table II. Fresh and Used Catalyst Analyses

Test Fe/Mn Ratio	SI-10 57/41		SI-12 94/56		SI-13 22/78		SI-15 10/90		SI-17 Fused-Iron	
	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used	Fresh	Used
Time on Stream, hr	---	166	---	237	---	309	---	223	---	118
Chemical Analysis, wt percent										
C	<0.1	11.6	---	13.4	<0.3	7.4	<0.3	2.9	<0.3	7.6
H	1.0	0.6	---	0.8	0.6	0.6	0.3	<0.3	<0.3	0.5
S	<0.07	<0.07	---	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07
K	<0.095	<0.095	---	<0.095	<0.095	<0.095	<0.095	<0.095	0.4	0.3
Fe	35.0	31.4	20.2	21.4	12.0	14.5	6.8	7.4	66.3	70.2
Mn	24.8	21.8	35.5	27.9	51.4	52.3	50.6	59.5	<0.095	0.1
DET Surface Area, m ² /g _w	150.0	29.2	121.5	22.6	76.5	31.7	59.9	25.5	1.3	1.6
Mean Pore Diameter, Å	40	216	72	103	93	103	100	224	---	300
X-Ray Diffraction										
Fresh	Mn ₂ O ₄ ^z	Fe ₂ O ₃ , MnCO ₃	Mn ₂ O ₄ ^z	Fe ₂ O ₃ , MnCO ₃	Mn ₂ O ₄ ^z	MnO ^a	Mn ₂ O ₄ ^z	MnO ^a	Fe ₂ O ₃	Fe ₂ O ₃
Used		unidentified minor phase		Minor FeC					Minor Fe ₂ O ₃	

Note: z = Fe may be present in solid solution with Mn₂O₄ or γ-Mn₂O₃.
 a = Fe may be present in solid solution with MnO.

for measuring particle size distributions indicated that the average particle size before and after each test was about 12 microns; SEM results in certain instances visually indicated smaller particle sizes for the fresh as well as used catalysts.

SUMMARY

Various compositions of iron-manganese catalysts were investigated in a slurry reactor for Fischer-Tropsch catalytic synthesis of hydrocarbons. Several conclusions can be stated:

- o All the iron-manganese catalysts tend to deactivate with time. Catalysts with the higher iron content had higher initial rates of deactivation.
- o As a function of time, the hydrocarbon product becomes more paraffinic, possibly due to hydrogenation of the primary olefins. Paralleling this is the isomerization of olefins, with a larger fraction of internal olefins as compared to terminal olefins being formed with time.
- o An increase in space velocity increased the olefin selectivity of the C₂-C₄ light gas, whereas an increase in temperature had an opposite effect.
- o Activation energies for synthesis gas reactions over the various iron-manganese catalysts ranged from 17-19 kcal/mole.

- o Analysis of the used catalysts indicate that deactivation could be caused by amorphous or graphitic carbon formation on the catalyst surface.

DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

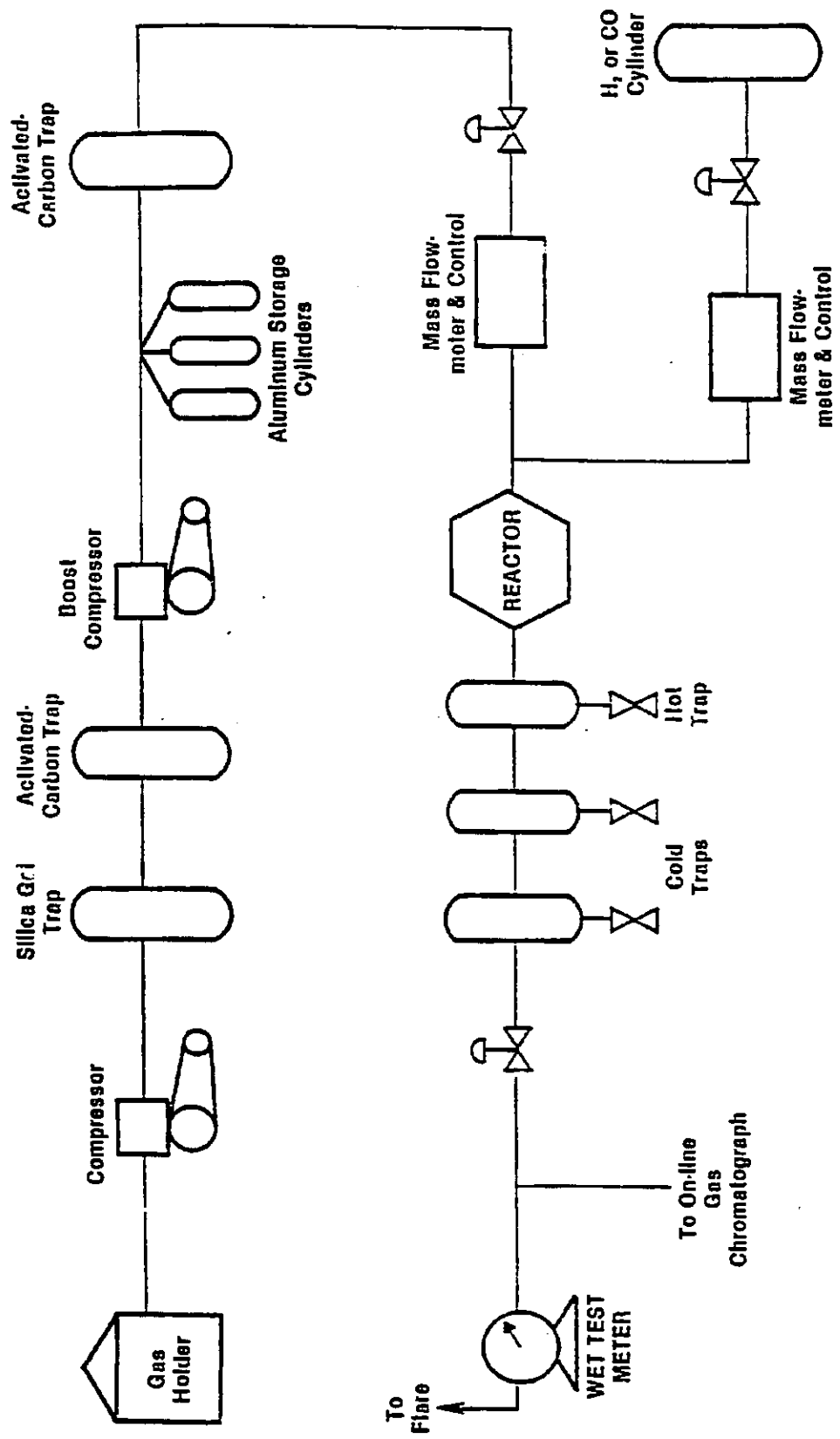
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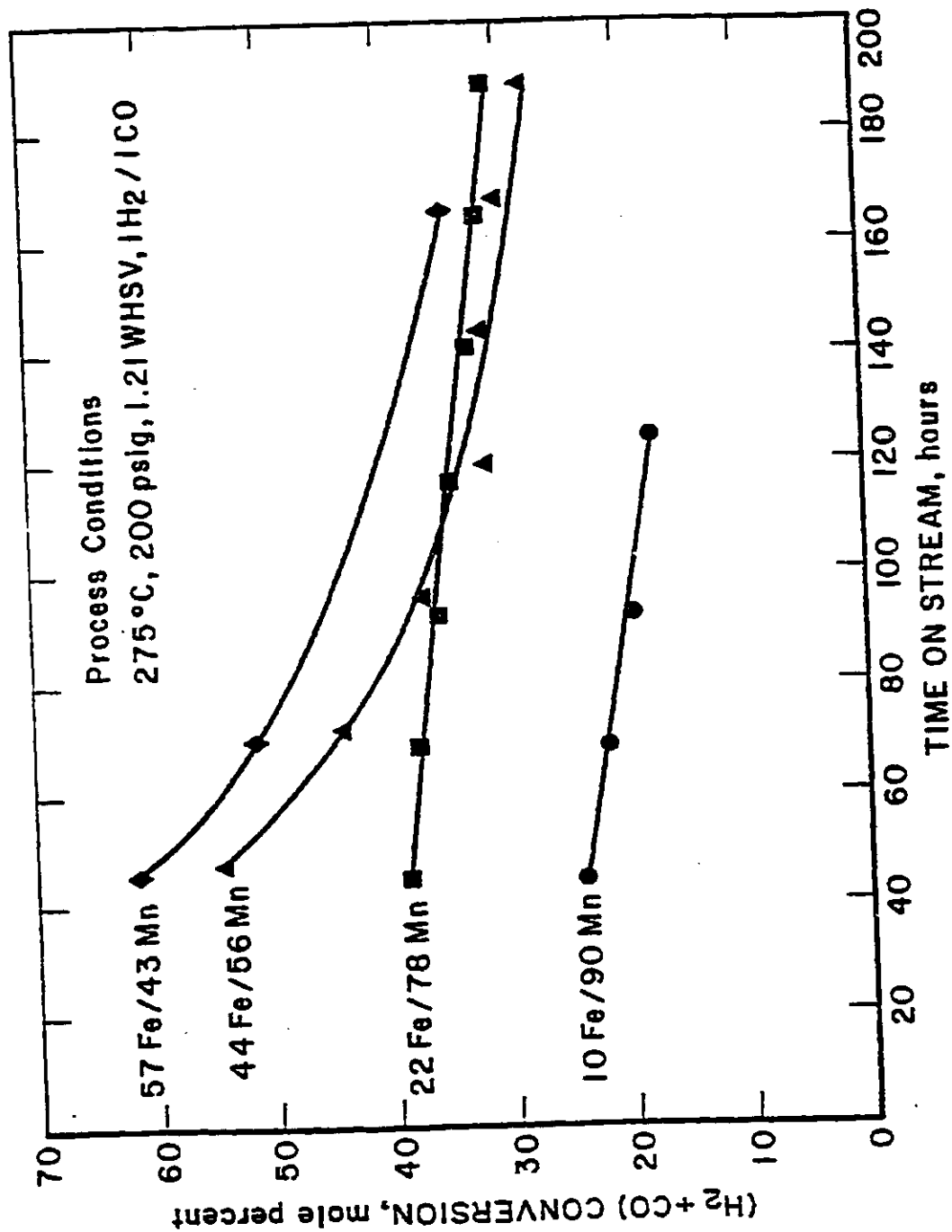
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FIGURE 1. SCHEMATIC OF REACTOR SYSTEM



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FIGURE 2. (H₂ + CO) CONVERSION OVER IRON-MANGANESE CATALYST AS A FUNCTION OF TIME