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TRANSPORTATION FUELS FROM SYNTHETIC GAS

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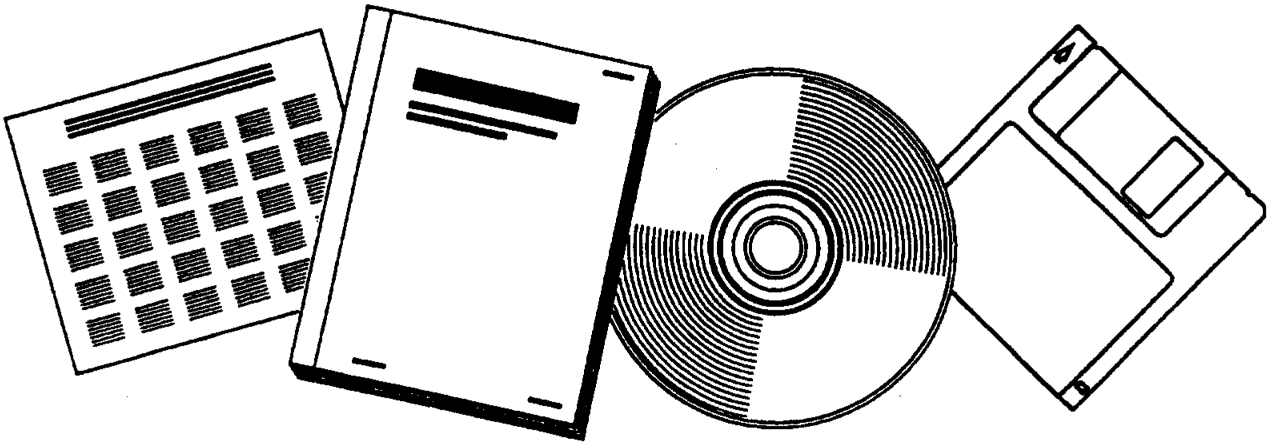

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Transportation Fuels from Synthesis Gas

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SUMMARY

Twenty-five experimental Fischer-Tropsch synthesis runs were made with 14 different catalysts or combinations of catalysts using a Berty reactor system. Two catalysts showed increased selectivity to transportation fuels compared to typical Fischer-Tropsch catalysts. With a catalyst consisting of 5 wt% ruthenium impregnated on a Y zeolite (run #24), 63-70 wt% of the hydrocarbon product was in the gasoline boiling range. Using a 0.5 wt% ruthenium on alumina catalyst (run #22), 64-78 wt% of the hydrocarbon product was in the diesel fuel boiling range. Not enough sample was produced to determine the octane number of the gasoline from run #24, but it is probably somewhat better than typical Fischer-Tropsch gasoline (~50) and less than unleaded gasoline (~88). The diesel fuel produced in run #22 consisted of mostly straight chained paraffins and should be an excellent transportation fuel without further refining.

The yield of transportation fuels from biomass via gasification and the Fischer-Tropsch synthesis with the ruthenium catalysts identified in the previous paragraph is somewhat less, on a Btu basis, than methanol (via gasification) and wood oil (PERC and LBL processes) yields from biomass. However, the products of the F-T synthesis are higher quality transportation fuels. The yield of transportation fuels via the F-T synthesis is similar to the yield of gasoline via methanol synthesis and the Mobil MTG process.

INTRODUCTION

Methods of producing liquid hydrocarbons from biomass fall into two general categories, direct and indirect liquefaction. Direct liquefaction methods include fermentation, thermochemical liquefaction, and pyrolysis. Biomass is converted indirectly to liquid hydrocarbons by converting it into a gaseous intermediate from which liquid fuels are synthesized. The two major syntheses are methanol synthesis and hydrocarbon synthesis via the Fischer-Tropsch (F-T) reaction. The F-T reaction produces the highest quality transportation fuels of any liquefaction method; however, a wide range of hydrocarbons are produced and significant separation and refining is required to make transportation fuels. The purpose of this study is to explore the use of bifunctional catalysts consisting of a group VIII metal supported on or mixed with zeolites or alumina to selectively produce high quality transportation fuels from synthesis gas.

Task 4 of PNL's Biomass Thermochemical Conversion Program Management Agreement includes in-house research and development activities to assist in fulfilling program objectives. This effort constitutes a portion of in-house research and development activities funded at PNL by the Biomass Thermochemical Conversion Program Office.

CONCLUSIONS AND RECOMMENDATIONS

These major conclusions are based on the results of this study:

- Increased selectivity to transportation fuels (gasoline and diesel fuel) compared to typical Fischer-Tropsch catalysts was obtained with two supported ruthenium catalysts (24RuY and 22RuAl). Synthesis gas conversion rates were similar to those obtained with typical Fischer-Tropsch catalysts.
- Although increased selectivity was not obtained with iron or cobalt supported catalysts, evidence suggests this is possible with the right choice of catalysts.
- The method of loading the metal on the support is critical, especially with the Y zeolite. Better selectivity was obtained when the ruthenium was impregnated on the zeolite by the "incipient wetness" method. This apparently deposited the ruthenium in the pores of the zeolite as opposed to the surface, as results from standard metal loading techniques.
- Time was not available to determine the lifetime of the catalysts or to obtain large enough samples for in-depth analysis of the products.
- The yield of primary product (gasoline or diesel fuel) obtained corresponds to 0.2 lb/lb dry wood based on synthesis gas from the BNW catalytic gasification process.

We recommend that investigation of selective production of transportation fuels from synthesis gas be continued along two different avenues:

- Long term test runs with catalysts 24RuY and 22RuAl. The purpose of these tests would be twofold: 1) provide some indication of the rate and selectivity of the catalysts versus time, and 2) produce enough liquid product for more in-depth analyses.
- Further investigation of other catalysts made by impregnation of a group VIII metals on zeolites by the "incipient wetness" method. By proper choice of metal and zeolite it should be possible to make

other selective catalysts. If a catalyst can be developed which can be operated at 300°C or over, increased isomerization and cyclization (higher octane) should result.

DISCUSSION AND RESULTS

The products of the Fischer-Tropsch synthesis range from C_1 to C_{30} hydrocarbons plus light oxygenates (alcohols and acids). Figure 1 shows the synthesis products with various operating conditions and catalysts. The liquid products peak in molecular weight distribution, then decline over a broad carbon number range. This has been likened to Shulz/Flory distribution of molecular weights frequently found in oligomerization and polymerization processes (Henrici-Olive 1976). Dry has shown that in both theory and practice the selectivity for gasoline (C_5-C_{12}) production peaks at about 40 wt% with conventional Fischer-Tropsch iron catalysts. Production of diesel fuel (C_{13}-C_{20}) peaks at about 18 wt% (Dry 1976).

Recently, increased selectively to gasoline and diesel fuel have been reported in the literature for various catalysts (Caesar 1979, Nijs 1979, Madon 1979, Fraenkel 1980). These catalysts are Ru, Co, and Fe combined with alumina or molecular sieve zeolites.

The liquid hydrocarbons from the Fischer-Tropsch are mainly normal paraffins and olefins. This makes for an excellent diesel fuel but results in poor quality gasoline (low octane). Significant refining is necessary to produce high octane gasoline. A potential solution to both the selectivity and octane problems is the use of polyfunctional catalysts. These catalysts would consist of a typical F/T metal supported on a zeolite or other acidic support. The metal component would catalyze carbon monoxide reduction and the zeolite component would play a catalytically active role (conversion of n-paraffins to isoparaffins or aromatics to increase the octane rating) and a passive (molecular sieving) role to improve selectivity.

At those conditions most suited for combination with biomass gasification, 200-500°C and 0-50 atm, conversion of paraffins to isoparaffins and aromatics is rate limited not thermodynamically limited. By combining a F/T catalyst with an isomerization catalyst it should be possible to increase the production of isoparaffins. The relative rates of some of the reactions involved is shown in Table 1.

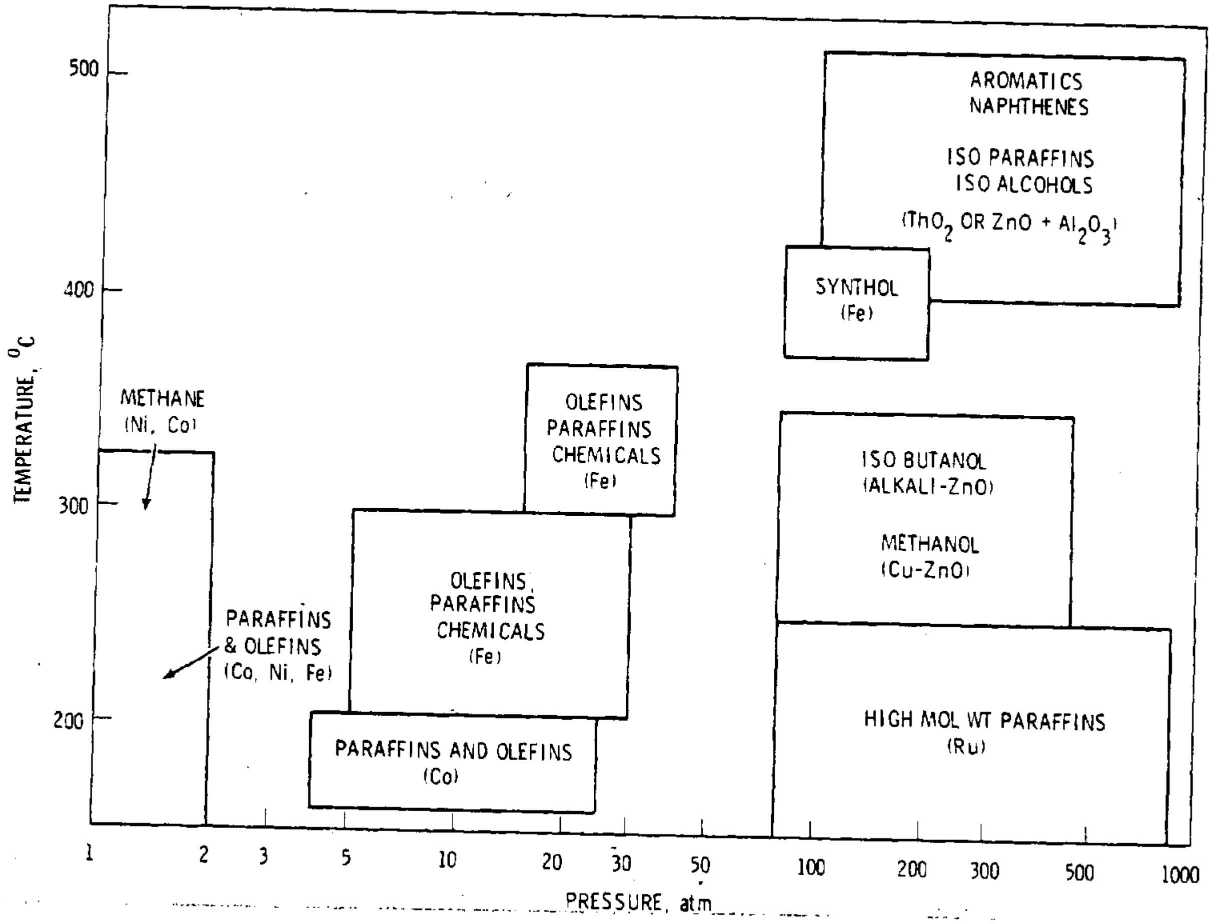

FIGURE 1. Products of Fischer-Tropsch Synthesis

TABLE 1. Relative Reaction Rates

Paraffin dehydrocyclization to aromatics	Slow[(a)]
Isomerization of paraffins (via olefins)	Rapid[(a)]
Paraffin dehydrogenatin to olefins	Very rapid[(a)]
Synthesis of paraffins from CO/H_2	Very rapid[(b)]

(a) with commercial catalytic reforming catalysts
(b) with commercial F/T catalysts

Commercial isomerization processes use Pt supported on alumina or a zeolite for a catalyst. Pt catalyzes the dehydrogenation of paraffins to olefins and the acidic support catalyzes isomerization of the olefins to branched chain compounds. Pt can also be used as a F/T catalyst, unfortunately, it is very selective towards methane production. Metals such as Co or Fe which are more selective towards liquid production in F/T synthesis also catalyze paraffin dehydrogenation. As this is not the rate-limiting step in producing isoparaffins, use of these metals may not affect the overall kinetics. Commercial isomerization units operate at 15-40 atm, 150-300°C, and space velocities similiar to F/T units.

Production of significant quantities of aromatics is probably only possible at high temperatures. Commercial catalytic reformers operate at 500-550°C. At these temperatures, however, methane is a major product of the F/T synthesis particularly at pressures under 50 atm.

The purpose of this study was to explore the use of bifunctional catalysts consisting of a Fischer-Tropsch metal supported on or combined with zeolites or aluminas to selectively produce high quality transportation fuels (gasoline and diesel) from synthesis gas. Synthesis conditions were limited to those most compatible with biomass gasification (200-500°C, 0-50 atm).

DESCRIPTION OF EXPERIMENTAL EQUIPMENT

A Berty gradientless, fixed bed, catalytic reactor manufactured by Autoclave Engineers was used for the synthesis gas conversion experiments. The reactor catalyst basket is 2.0 in. (5.08 cm) in diameter, 2.0 in. (5.08 cm) tall and holds approximately 60 cc of catalyst maximum. The reactor has an internal gas recycle system and at high recycle rates it is equivalent to a continuous stirred-tank reactor. A temperature controller maintains the temperature in the catalyst bed at the desired setpoint by adjusting the output of the ceramic furnace in which the reactor is enclosed.

Hydrogen and carbon monoxide are fed from cylinders at up to 500 psig. Gas flow rates are measured with Matheson Model 8240 mass flow indicators. Whitey metering valves are used to control gas flows and the reactor pressure. The product gas leaving the reactor passes through a condensor and a gas/liquid separator. The gas from the separator passes through a wet test meter and is vented into a hood. Figure 2 is a flow diagram for the system.

The gaseous and liquid products were analyzed with a Hewlett Packard 18850A and a Carle AGC-S gas chromatographs. Table 2 shows the conditions used for analysis of each product.

REACTOR INSTALLATION AND SHAKEDOWN

The catalytic reactor system described earlier was installed in October and November 1980. We pressure checked the system to 500 psig with nitrogen. Several leaks were discovered and repaired. The first run with catalyst and synthesis gas was made on December 3, 1980. Numerous problems with the reactor system and the analytical support equipment were encountered on this run and succeeding runs. Some of the major problems that occured are listed below:

1. The reactor temperature control unit did not function properly and the vendor replaced it free of charge.
2. Three different product gas lines and condensers were used before accurate material balances were obtained. Wax buildup in this system made accurate material balances impossible and caused plugs on occasion.
3. The flowmeters were too large for the gas flows required and had to be adjusted and recalibrated.
4. Some of the metering valves in the system were too large for good control and were replaced with smaller valves.
5. We had several problems with sampling techniques and gc analysis which were corrected by trial and error.
6. The internal recycle fan in the reactor had to be realigned to prevent it from scraping the catalyst basket.

The first run for which a complete set of data was obtained was on January 28.

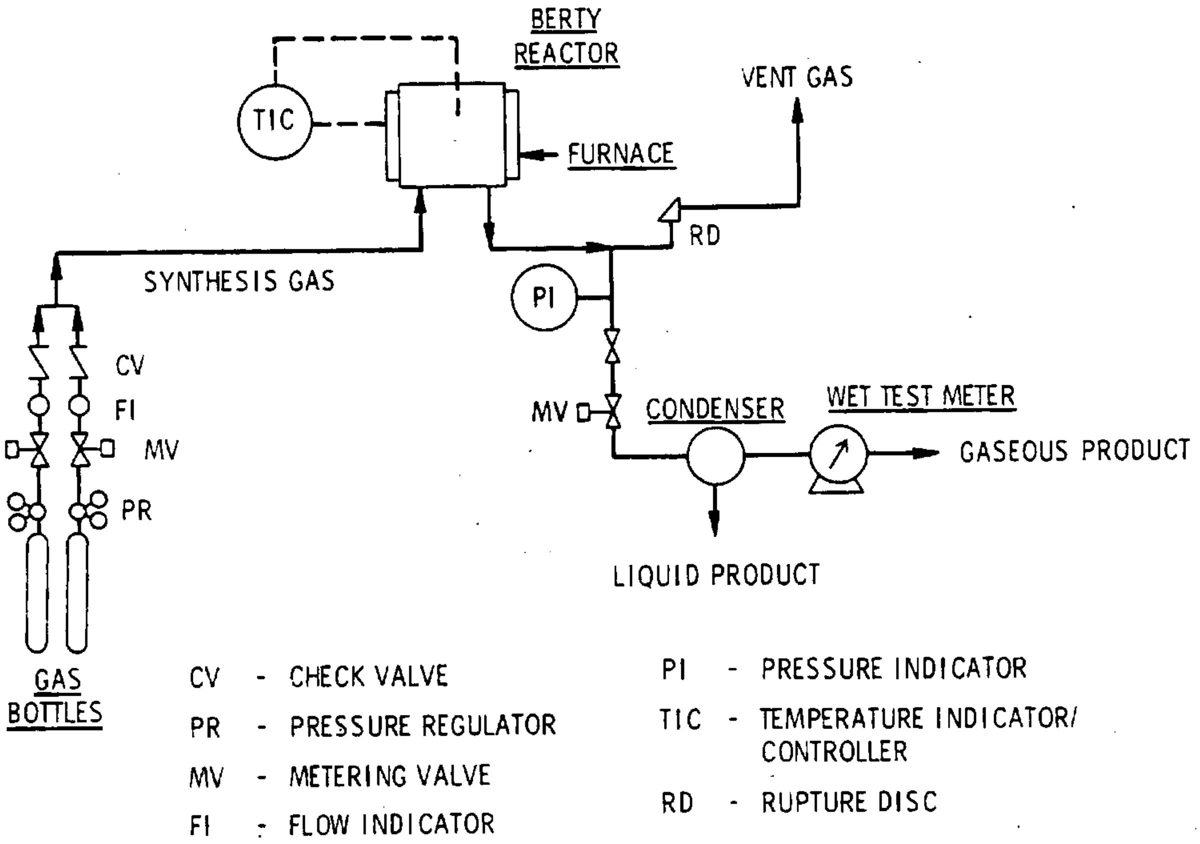

FIGURE 2. Synthesis Gas Conversion Reactor

CATALYST PREPARATION AND REDUCTION

The catalysts we selected for study fall into three main categories:

1. Some commercially available iron, cobalt, and ruthenium catalysts known to be active for the F-T synthesis
2. Two component catalysts consisting of a mixture of commerically available F-T catalysts and commercially available zeolite catalysts
3. Catalysts prepared at PNL by loading group VIII metals on commerically available zeolites.

Many group VIII metals are active for the Fischer-Tropsch synthesis. We selected iron, cobalt, and ruthenium based on their known activity for production of liquid hydrocarbons (Borghard 1979).

TABLE 2. Chromatographic Conditions

	Phase		
	gas	gas	liquid
Gas Chromatograph	Carle AGC-S	Hewlett Packard 18850A	Hewlett Packard 18850 A
Column	Integrated system with six columns	Porapak Q	5% SE-30 on Chromosorb
Carrier Gas	Helium	50 ml/min N_2	50 ml/min N_2
Detector	TCD	FID	FID
Detector Temperature, °C	50	280	280
Injector Temperature, °C	Ambient	280	280
Column Temperature, °C	50	40-250	40-250
Ramp, °C/min	-	15	15
Compounds	H_2, CO, CO_2 CH_4, C_2H_4, C_2H_o, O_2, N_2	C_1-C_{10} hydrocarbons	C_5-C_{30} hydrocarbons

Molecular sieve Y zeolites and alumina were selected as support materials to be used. Both are common support materials and the Y zeolites are known to be catalysts for isomerization of normal paraffins (King 1978). Table 3 lists the catalysts that were used in each run in which we achieved significant conversion of synthesis gas to liquid product.

Two different metal loading procedures were used to load iron and ruthenium on Y zeolites. Metals were loaded by ion exchange by slurrying the zeolite in deionized water and adding a metal salt solution (Linde). Metals were also impregnated on zeolites using the "incipient wetness method".

TABLE 3. Description of Catalysts

Run #	Catalyst Description	Preparation	Reduction
9	Triple promoted fused iron 4/14 mesh	United Catalyst C-73-1 (~70% Fe)	24 hrs at 450°C, H_2 GHSV = 1200
10	Triple promoted fused iron 4/14 mesh (33 vol%) + Y zeolite 1/16" pellets(67 vol%)	United Catalyst C-73-1 (~70% Fe) Linde LZY82	24 hrs at 450°C, H_2 GHSV = 1200
11	5.0% Ruthenium on Y zeolite 6/14 mesh	Ion exchanged Ru Cl_3 solution (Strem) with Linde LZY82	3 hrs at 325°C, H_2 GHSV = 800
12	Cobalt on Kieselguhr 4/14 mesh (33 vol%) + Y zeolite 1/16" pellets (67 vol%)	United Catalysts G-67C Linde LZY82	4 hrs at 400°C, H_2 GHSV = 1200
13	Triple promoted fused iron 4/14 mesh(20 Vol%) + A zeolite 1/8" Pellets (80 Vol%)	United Catalyst C-73-1 Linde AW-500	24 hrs at 450°C, H_2 GHSV = 1200
14	~0.5% ruthenium on Y zeolite 6/14 mesh	Ion exchanged $RuCl_3$ solution (strem) with Linde LZY82	3 hrs at 325°C, H_2 GHSV = 1100
16	~0.5% ruthenium on Y zeolite 6/14 mesh	Ion exchanged $RuCl_3$ solution (strem) with Linde LZY52	3 hrs at 325°C, H_2 GHSV = 1100
17,22	~0.5% ruthenium on alumina 1/8" pellets	Strem Chemicals	3 hrs at 325°C, H_2 GHSV = 1100
23	Iron on Y zeolite 1/16" pellets	$Fe(NO_3)_3$ (Mallinkrodt)(a) impregnated on Linde LZY82	18 hrs at 450°C, H_2 GHSV = 1300
24,25	Ruthenium on Y zeolite 1/16" pellets	$RuCl_3$ (Strem) impregnated(a) on Linde LZY82	4 hrs at 450°C, H_2 GHSV = 1200

(a) Zeolites impregnated by "incipient wetness". A metal salt solution containing enough metal to impregnate 5 wt% metal on the zeolite was used; however, not all of the metal was impregnated, particularly for the iron catalyst.

EXPERIMENTAL RESULTS

A review of past investigations of the Fischer-Tropsch synthesis led to the choice of 250 psig (17 atm) as the operating pressure for all experiments (Storch 1951, Anderson 1956, Vanice 1976, Shah 1976, Field 1960, Garrett 1960, and Borghard 1979). Operating temperature for maximum gasoline production was 300-340°C for iron catalysts, 220-260°C for ruthenium catalysts, and 190-210°C for cobalt catalysts. Space velocities were adjusted to achieve reasonable conversion and ranged from 650-2340 GHSV. The results of all runs in which a significant conversion of synthesis gas to liquid hydrocarbon was achieved are shown in Table 4.

Selectivity

Run 9 is typical of iron catalyzed F-T synthesis for maximum gasoline production. The results are similar to the synthol process used at SASOL in South Africa with 40 wt% of the product in the gasoline boiling range (Dry 1976). In runs 10 and 13 we mixed the triple-promoted iron catalyst with Y and A zeolites, respectively. The product distribution was very similar to run 9. An ion exchange procedure was used to load ruthenium on a Y zeolite for runs 11 (5 wt%) and 14 and 16 (0.5 wt%). Over 50 wt% of the hydrocarbon product was in the C_5-C_{12} range, a small increase compared to the iron catalysts. For runs 24 and 25, approximately 5 wt% ruthenium was impregnated on a Y zeolite by the "incipient wetness" method (from here on referred to as catalyst 24RuY). Over 70 wt% selectivity to C_5-C_{12} hydrocarbons was obtained early in run 24. This decreased and leveled off at 65-70 wt% as the run progressed. In run 25 gasoline selectivity was somewhat less, 57-65 wt%. In all other runs gasoline selectivity was less then 40 wt%.

Impregnating the ruthenium on the zeolite by the "incipient wetness" method apparently deposits the ruthenium in the pores of the zeolite as opposed to the surface which results from standard metal loading techniques (Nijs 1980, Bosi 1979). Researchers in Belgium recently reported similar results for ruthenium catalysts supported on Y zeolites (Nijs 1979).

TABLE 4. Results of Fischer-Tropsch Synthesis Experimental Runs

Run #	9D	10B	11A	11B	12	13A	13B	14A
Date	1/28	2/5	2/10	2/10	2/12	2/19	2/20	2/24
Catalyst	Iron	Iron +LZY82	Ru on LZY82	Ru on LZY82	Cobalt +LZY82	Iron +A zeolite	Iron + A zeolite	Ru on LZY82
Temperature, ^{o}C	338/215	340/313	250/235	266/252	196/188	332/314	345/327	250/241
Pressure, atm	17	17	17	17	17	17	17	17
Space Velocity GHSV	2340	1588	1330	1330	650	783	783	567
H_2/CO Ratio	2.1	2.2	2.0	2.0	2.1	1.9	1.9	2.0
CO Conversion, %	87	86	80	79	18	87	83	54
H_2 Conversion, %	47	43	80	87	12	48	45	54
Usage Ratio	1.2	1.1	2.0	2.2	1.4	1.0	1.0	2.0
Total Conversion, %	60	56	80	84	14	61	58	54
Rate cc gas conv/cc catalyst/hr	1404	851	1064	1117	91	478	454	306
g gas conv/g metal/hr	0.41	0.72	11.6				0.63	39.7
Hydrocarbon yield g/m^3 H_2+CO converted	204	208	197	184	208	213	204	212
Hydrocarbon Distribution, wt%								
C_1-C_4	32	42	26	47	17	32	42	32
C_5-C_{12}	43	38	53	37	31	36	33	49
C_{13}-C_{20}	22	16	17	13	41	27	18	14
C_{20}^+	5	4	4	3	11	6	8	5

TABLE 4. (continued)

Run #	14B	16	17	22A	22B	23	24	25
Date	2/24	3/4	3/6	3/27	3/27	3/31	4/2	4/8
Catalyst	Ru on LZY82	Ru on LZY52	Ru on Alumina	Ru on Alumina	Ru on Alumina	Iron on LZY82	Ru on LZY82	Ru on LZY82
Temperature, ^{o}C	275/264	250/239	223/216	220/214	245/240	277/275	238/232	240/230
Pressure, atm	17	17	17	17	17	17	17	17
Space Velocity GHSV	567	926	750	1061	1061	856	741	693
H_2/CO Ratio	2.0	2.1	1.85	2.0	2.0	2.0	1.8	1.9
CO Conversion, %	50	28	50	25	49	65	77	83
H_2 Conversion, %	54	24	48	21	51	63	87	90
Usage Ratio	2.2	1.8	1.8	1.7	2.1	1.9	2.0	2.1
Total Conversion	53	25	49	22	50	64	83	88
Rate cc gas con/cc catalyst/hr	301	234	365	237	530	548	618	610
g gas conv/g metal /hr		36.6	24.0			8.3	16.4	
Hydrocarbon Yield g/m^3 H_2+CO converted	185	212	216	215	193	180	189	189
Hydrocarbon Distribution, wt%								
C_1-C_4	43	22	5	11	13	69	15	26
C_5-C_{12}	35	51	29	29	27	14	70	63
C_{13}-C_{20}	14	24	53	58	50	15	15	11
C_{21}+	8	3	12	3	10	1	0	0

A commercial 0.5 wt% ruthenium on alumina catalyst (from here on referred to as catalyst 22RuAl) showed a high selectivity to diesel fuel (C_{10}-C_{20}) in runs 17 and 22. Between 64-77 wt% of the hydrocarbon product in these runs was in the diesel fuel range. This is similar to results obtained by Madon with a 1% ruthenium on alumina catalyst (Madon 1979).

Product Quality

The quantity of liquids produced were not sufficient for octane tests so the anti-knock properties of the gasoline fractions can be compared only qualitatively. Table 5 shows the ratio of branched C_{10} compounds to straight-chained C_{10} compounds for several runs.

Addition of Y and A zeolites to the triple promoted iron catalyst produced some increase in isomerization (runs 10 and 13) compared to the iron alone (9D). Ruthenium impregnated on a Y zeolite resulted in the highest degree of isomerization (run 24) although it deteriorated throughout the run. The lowest degree of isomerization was in run 22A. However, most of the liquid produced in this run was in the diesel fuel range. Diesel fuel requires a low octane (high cetane number) and the diesel fraction produced in 22A should be an excellent diesel fuel without additional refining.

Rate of Conversion

The rate of conversion for each run is shown in Table 4. The first numbers given are volumes of $2H_2$+CO synthesis gas converted per volume of catalyst per hour. The highest rate of conversion was for the triple promoted fused iron catalyst followed by the 5% ruthenium on Y zeolites, mixtures of iron plus Y and A zeolites, 0.5% ruthenium on Y zeolites and alumina, and the cobalt/kieselguhr catalyst. For several runs the rate was calculated in terms of grams of synthesis gas converted per gram of metal per hour. When the rate of conversion is expressed in these terms the 0.5% ruthenium on Y zeolites and alumina have the highest rate of conversion followed by 5% ruthenium on Y zeolites. The triple promoted iron and mixtures of iron and zeolites had the lowest rate of those catalysts for which the rate was calculated in this manner.

Table 5. Comparison of Branched and Straight-Chain Compounds

Run #	9D	10B	11A	13B	22A	24	
iC_{10s}/nC_{10}	0.75	1.33	0.51	0.97	0.13	3.27[(a)]	(1.43)[(b)]

(a) after 2 hr
(b) after 5 hr

PROCESS CONSIDERATIONS

Based on results of run 24 and data from the BNW catalytic gasification proess demonstration unit (Mudge 1981), approximately 0.2 lb of C_5-C_{12} material would be produced per lb of dry wood with catalyst 24RuY. By-products would be 0.04 lb of C_1-C_4 and 0.04 lb of C_{13}-C_{20}. The results of run 22A combined with data from the catalytic gasification system indicate 0.21 lb of diesel would be produced per pound of dry wood with catalyst 22RuAl. By products would be 0.03 lb C_1-C_4 0.05 lb C_5-C_9 and 0.01 lb C_{21}-C_{25}.

These results are compared to other methods of producing liquid fuels from wood in Table 6. The expected yield of gasoline is similar to the expected yield of gasoline via oxygen-blown gasification, methanol synthesis and the Mobil MTG process (Kam 1979). The yield based on heating value is only 60-80% of that for methanol production via the BNW catalytic gasification process and 70-95% of the yield from direct liquefaction processes. However, the products from the Fischer-Tropsch synthesis are higher quality fuels. The diesel fuel (catalyst 22RuAl) could be used directly without further refining. The gasoline (catalyst 24RuY) would probably require some octane improvement prior to use as a transportation fuel.

TABLE 6. Liquid Fuels from Wood

	Major Product Only lb liquid/lb dry wood	Major Product	Btu/lb dry wood
Perc Process (Wilhelm 1980)	0.42 0.33	heavy fuel oil	5670 4460
LBL Process (Wilhelm 1980)	0.32 0.27	heavy fuel oil	4960 4190
Gasification/Methanol (BNW) (Mudge 1980)	0.50 0.58	methanol	5150 5970
Gasification/Methanol (Oxygen-blown) (Kam 1979)	0.52	methanol	5360
Gasification/Methanol/Gasoline (Oxygen-blown) (Kam 1979)	0.20	high octane gasoline	4000
Gasification (BNW)/F-T (Catalyst 24RuY)	0.20	gasoline	4000
Gasification (BNW)/F-T (Catalyst 22RuAl)	0.21	diesel	4000

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