ATTACHMENT XIV

Review of Fischer-Tropsch Work by Rentech

Rentech has obtained eight patents to date [October 10, 1996] [XIV.1-XIV.8]. The drawings, background of the invention and objectives of the invention are identical [except for combining some paragraphs and minor changes in a few paragraphs such as "A further object ..." rather than "It is yet another objective..."]

The background provides a brief description of earlier work [XIV.9-XIV.14]. They indicate that today there are two primary methods for producing syngas from methane: steam reforming and partial oxidation. The primary advantage of partial oxidation over steam reforming is indicated to be that the reaction is self-sustaining and the only heat that must be added is the initial preheating of the reactants. Another advantage is that a lower ratio of H_2/CO is produced, and that it more nearly matches that needed for the FTS. In addition, the CO_2 and/or hydrogen need not be removed from the syngas prior to the synthesis.

The authors indicate that "...the Fischer-Tropsch reactor must typically be able to convert at least 90% of the incoming carbon monoxide."

They discuss the advantages of the two materials they consider to be attracting the most attention: cobalt and iron based catalysts. They indicate that, theoretically, a cobalt catalyst can produce higher conversion yields than an iron based-catalyst since the cobalt catalyst can approach 100% carbon conversion efficiency but that an iron catalyst tends toward 50% carbon conversion to hydrocarbons due to the extent of the water-gas-shift (WGS) reaction. They indicate that cobalt is much higher in cost, and this is likely to increase even further if the demand for cobalt increases to meet widespread development of Fischer-Tropsch synthesis (FTS).

XIV.1-Draft

It is indicated that recycle of the tail-gas is usually utilized to achieve 90% conversion of CO. Too much water is considered to be an inhibitor for FTS and the maximum attainable in single-pas operation is 70% CO conversion. On the other hand, the WGS activity of the iron catalyst permits operation at 90% conversion per pass without difficulty. It has been reported, contrary to this view, that even with an iron catalyst, the rate of CO conversion may decline rapidly at CO conversions above about 60% [XIV.15].

The present inventions are claimed to "...include a solution to the problems of reducing the formation of excess hydrogen from the reformer or partial oxidation unit and increasing the conversion efficiency for the entire carbon input to the system when using specifically prepared promoted iron catalysts." The patents demonstrate the use of recycle of the carbon dioxide produced during the FTS to the reformer in order to control the excess hydrogen and to improve the carbon conversion efficiency problems.

It is stated that olefins, alcohols and aldehydes are readsorbed on the catalyst and thereby participate in further chain growth. Naphtha and light diesel fractions are considered to be rich in olefins and to contain relatively large amounts of alcohols. Thus, the authors indicate that it is possible to force the reaction toward higher molecular weight by recycle of olefins, alcohols and aldehydes.

It is also proposed to convert the excess hydrogen as well as the carbon dioxide that is produced through the WGS reaction in a second FTS reactor.

A schematic of one of the process schemes is provided in figure 1. Indicated in this process is the recycle of carbon dioxide and/or recovered gas (streams 9 and 19).

The preferred catalyst is a precipitated iron catalyst that is promoted with a predetermined amount of potassium and copper. The amount of promoters depends upon the desired extent of chain growth and the product molecular weight distribution.

The preferred catalyst is unsupported. To accomplish catalyst preparation, iron and copper metal is dissolved in nitric acid. However, to minimize the emission of oxides of nitrogen, oxygen is bubbled through the solution while the metals are being dissolved.

The catalyst precursor was prepared by precipitation by the addition of ammonium hydroxide (ambient temperature) to the hot (up to 150°C copper/iron solution to produce a pH of 7.4. After cooling to 80°F, the pH is adjusted to 7.2. The slurry is pumped to a holding tank, the solid settles and the solution is removed; subsequent washings to remove ammonium nitrate are with "high quality water free of chloride". A drum filter, with water spray bars, is used to complete the washing and collection of the slurry. Aqueous potassium carbonate of the desired amount is added to the slurry and it is then thoroughly mixed. Drying, such as in a spray drier, is used to produce spherical catalyst in the size range of about 1 to 5 up to about 40 to 50 microns. The last step is heating to 600°F in a fluidized bed to remove residual moisture and to convert the hydrous iron oxide to hematite (Fe_2O_3).

The authors report that "Determining the "best" activating procedure for a catalyst is difficult at best..." In their study, high activity of the catalyst was correlated with the presence of iron carbides after the activation procedure. The most effective procedure used carbon monoxide at 325°C at 0.1 atm. pressure. The authors indicate that it may be preferable to activate in synthesis gas, and give a recipe for doing this in a controlled manner. They heat the catalyst precursor in an inert gas to 500°F and then

to 540°F in synthesis gas until the heat of reaction becomes sufficient to heat the catalyst bed at a faster rate than the applied external heat; at this point heating is terminated and cooling is effected to keep the temperature at 540°F until the CO conversion is 90%. At this point the temperature is lowered to the desired reaction temperature (450 to 525 °F) and the reactor pressure is raised from the activation pressure of 150 psig to below about 450 psig. The flow rate is adjusted to a space velocity in the range of 240 to 300 per hour.

It was reported that the activity and selectivity of the iron catalyst is improved by exposure to a hydrogen-rich synthesis gas at elevated temperature and pressure. The production of water is believed to prevent over-carburization of the catalyst, and thereby inducing the improved activity and selectivity [XIV.16].

The authors prefer a reactor design similar to that utilized by Bureau of Mines workers [XIV.17]. The gas distributor may consist of orifices or of porous metal spargers. Preferably a design using concentric rings of manifolds arranged to conform to the reactor; i.e., the largest diameter ring is at the highest and the smallest diameter at the bottom of the reactor. The reactor diameter should be selected to give a superficial velocity (actual volumetric flow rate of feed gases divided by empty reactor cross-sectional area) between about 0.02 to 0.2 meters per second. This flow should expand the bed by 30 to 45% over that of no flow conditions.

The authors prefer between 5 and 15 wt.% by weight of iron in the slurry, more preferably between 7.5 and 12.5, and most preferably 10 wt.% iron. This corresponds to 30 to 90 grams of iron per liter of expanded bed, and the most preferred is 60 g/L.

Heat removal utilizes heat exchanger tubes that commence about 1 meter above the gas distributor and extends to the top of the expanded slurry. Pressurized steam is the preferred heat transfer medium.

The preferred iron catalyst particle is between 10 and 40 microns, with 30 microns being most preferred. The preferred ratio of potassium (as carbonate) to iron is about 0.010 (0.005 and 0.015). The copper to iron ratio is preferably about 0.010.

The means of removing wax from the catalyst employed a cross flow filter. The advantage of this means is that the flow velocity of the slurry through the porous filter tubes is about 10 feet/sec and this slows down the rate of building a catalyst layer on the tube wall. When the flow has declined to a predetermined level, an inert gas is used to pressurize the shell side to remove the layer of catalyst into the slurry stream, which flows back to the reactor. They described rates for a cross-flow filter from Mott Metallurgical Corp., a filter and procedure which were found to be unsuitable for the operation at the LaPorte, Texas plant.

Catalyst can be removed from the reactor periodically by employing a slipstream.

The gaseous product stream (20, figure 1) can be used directly for process heat.

The quality of the diesel obtained from the Fischer-Tropsch synthesis are illustrated in Tables XIV.1 and XIV.2.

According to the data, the material contains 3.05 wt.% oxygen and the average carbon number is C_{14}. Assuming that the oxygen is distributed on the same basis as the hydrocarbons, then we calculate that the F/T diesel must contain about 38 wt.% alcohols in order to contain 3.05 wt.% oxygen. This value for the alcohol content appears consistent with the composition included at the bottom of Table V of U.S.

Patent 5,324,335. This would appear to be the highest content of alcohols that has been reported for Fischer-Tropsch products.

One of the catalysts utilized in the studies produces a chain-growth probability of 0.73 for carbon numbers from 1 to 9. Like Satterfield and coworkers, the patents reported that two different chain-growth probabilities were obtained.

In example 1, the authors indicate a means of calculating the carbon conversion efficiency for the overall process which is defined as the rate of production of carbon contained in the C_{5+} product in the FTS divided by the carbon atoms in the process feed. The authors state that, "Table VIII lists the product yields and carbon efficiency along with operating parameters for Example 1 and several examples discussed below." However, Table VIII does not contain a column giving efficiencies and the yield given in Table VIII is for C_{7+} rather than C_{5+} as given in the definition. It is not obvious how one can obtain the efficiencies, as defined, from the data in Table VIII. Efficiencies are given in some of the examples together with some indication of the mode of recycle; these are complied in Table XIV.3 by the reviewer.

The carbon dioxide produced in the FTS can be recovered by absorption from the FTS tail gas and can then be recycled to the gasifier, vented to the atmosphere or stored for later sale or use.

When additional diesel fuel is desired, the wax can be heated to 410°C to effect thermal cracking. It was shown that the diesel from wax cracking contained only 0.16% oxygen whereas the diesel produced in the FTS contained 3.05% oxygen.

After removing the carbon dioxide, the tail gases from the FTS can be recycled to the FTS reactor to "...enable further chain growth of olefins and alcohols."

Examples 2 through 11 were ..."modeled using the conditions listed. The modeling is based on the experience with various conditions used in pilot plant studies and represents the expected results using the conditions employed."

In Example 2, the authors write that, "The large carbon dioxide content (approximately 18%) of the gases leaving the separation vessel is undesirable for the synthesis reactor feed. Therefore, the next step in synthesis gas preparation is reduction of the carbon dioxide content to less than about 5% by volume, and in the example to less than 2%."

Examples 3-10 involve various carbon dioxide and/or light gas recycle and some of these results are summarized in Table XIV.3.

In example 11 it is stated that, "...it was found that the tail gases from the Fischer-Tropsch reactor which consist chiefly of hydrogen and carbon dioxide can be converted to liquid hydrocarbons in a second Fischer-Tropsch reactor... A test was conducted in a small slurry reactor using the same iron-based catalyst that was used in the Fischer-Tropsch synthesis. The temperature, pressure and space velocity were also kept the same. The carbon dioxide conversion was 25% for a feed having hydrogen to carbon dioxide ratios of 2:1 and also 1.5:1. Conversion of the hydrogen was 42%, and 88% of the carbon monoxide produced in the water gas shift reaction was converted to hydrocarbons in the Fischer-Tropsch reaction. The chain growth (a) was the same as in the conventional Fischer-Tropsch synthesis."

Apart from the claims, references XIV.1, XIV.6 and XIV.7 are essentially identical. The patent of reference XIV.1 claims the production of an oxygen containing diesel fuel using FTS. The claims in references XIV.6 and XIV.7 cover a variety of

carbon dioxide and/or light gaseous product recycle schemes that include both stream(s) and the fraction of each stream to be recycled.

Another grouping of three patents are essentially identical except for the claims [XIV.2-XIV.4]. These three patents are to show, "Several Fischer-Tropsch reaction schemes using a promoted iron catalyst in a slurry reactor produce oxygenated naphtha and diesel fractions on distillation that reduce particulate emissions in diesel engines. High carbon conversion efficiencies and optimum chain growth are characteristics of the process."

These three patents are identical to the above three patents up to the Detailed Description of the Invention and, apart from the one difference described below, this section is the same in the two sets of three patents. In references XIV.2-XIV.4 the paragraph in references XIV.1, XIV.6 and XIV.7:

"The steam reforming reactor 5 can be of conventional design employing a commercial nickel catalyst such as obtained from Katalco and designated **23-1**. Preferably, the reactor should be operated at from about 1292°F (700°C) to about 1652°F (900°) at system pressure of about 12 psia (82.7 kPa) to about 500 pais (3447 kPa). The flow of input gases through the reactor catalyst bed should be approximately 300 lbs/hr/ft^3 catalyst."

has been replaced by examples of approaches to reduce the amount of carbon monoxide in town gas to a specified level, for example 10% by volume.

It is shown that the water gas shift reaction could be used to reduce the level of CO in the output from the gasifier; however, this approach significantly reduces the heating value of the resulting town gas. It is shown that the removal of the CO_2

produced during the WGS will increase the heat content of the town gas but, in order to have 10% CO in the product, the extent of WGS must be even greater.

The objective of these patents [XIV.2-XIV.4] is to replace the shift reactor with a FTS reactor to remove the excess CO. Thus, a portion of the gas from the gasifier is fed to the FTS reactor while about 20% of the gas bypasses the FTS reactor (Case III in ref. XIV.2-XIV.4). The composition of the blending streams and the town gas are shown in Table XIV.4.

In addition to the town gas, the FTS produces 11.8 barrels of hydrocarbon liquids having five or greater carbon atoms (based on 1.0 MMSCF feed from the gasifier).

Removing the CO_2 will permit the heating value of the town gas of Case III to be increased but this will require a greater fraction of the effluent from the gasifier passing through the FTS reactor (Table XIV.5).

In this instance 12.6 barrels of C_{5+}-hydrocarbons will be obtained.

In another scenario, a WGS reactor is included in the process that can be utilized when the FTS reactor is inoperable or, in another scenario, both the FTS and WGS reactors can be utilized in parallel.

The catalyst activation and the test results of this group of three patents [XIV.2-XIV.4] are identical to those in the first group of three patents [XIV.1,XIV.6,XIV.7]. The examples in references XIV.2-XIV.4 are essentially the same as those in references XIV.1, XIV.6 and XIV.7.

Reference XIV.2 claims a method of thermally cracking a wax produced by a FTS reaction using an iron-based catalyst in a slurry reaction at a temperature of 770°F (410°C) for a sufficient period of time to produce diesel and naphtha fractions.

Reference XIV.3 claims a method for preparing and activating with synthesis gas a material that is catalytically active for Fischer-Tropsch synthesis.

Reference XIV.4 claims a FTS method suitable for producing a diesel product that is cleaner than commercially available that is derived from crude oil and having a cetane number which is higher than 45 and aromatics less than 1% and the same product that contains more than 2 wt.% oxygen.

The final two patents [XIV.5,XIV.8] are essentially identical to each other and, except for a section describing the use in conjunction with power generation and the claims, are identical to references XIV.2-XIV.4. The Fischer-Tropsch processes are used in combination with electric power generation. The example considers a 300 MW off-peak power production rate (during 17 hours of the 24 hour day) in a plant with a thermal efficiency of 33%. The feed gas requirements for the peak and off-peak conditions are 14.87 and 11.15 million standard cubic feet per hour (MMSCFH), respectively. This requires a FTS reactor to handle 3.72 MMSCFH of coal gas during off-peak hours. To prevent slurry bed slumping, the FTS reactor would require an additional 0.45 MMSCFH during peak operation. During peak operation, the FTS conditions would be changed from 250 to 100 psi to maintain an adequate superficial velocity in the FTS reactor. The average production of liquid hydrocarbons would be about 2100 barrels per day.

Reference XIV.5 claims: (1) a FTS process for producing liquid hydrocarbons from a synthesis using an iron catalyst in a slurry reactor with recycle of CO_2 to the gasifier, (2) claim 1 using coal derived synthesis gas and (3) the method of claim 2 wherein the FTS is used in combination with an electric power generation system.

Reference XIV.8 has one claim for a diesel fuel additive for reducing particulate emissions by utilizing the oxygenates in the FTS product so that the diesel contains at least 2 wt.% oxygen.

The discussion in the sections of these patents provides an excellent overview of FTS using an iron catalyst and of process concepts to improve the efficiency of carbon utilization. At times it is difficult for the reader to easily discern whether the data is from modeling or produced by experiment. Rentech has operated a 6-inch 8-foot tall slurry reactor both with and without CO_2 removal in advance of the FTS reactor [XIV.8]. In 1992 it was reported that the longest run was for a two-week period but it is understood that subsequent runs have been made for periods of 60 days or more; however, data for these longer runs do not appear to be available in the public domain.

REFERENCES

XIV.1. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons," U.S. Patent 5,324,335, June 28, 1994.

XIV.2. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons," U.S. Patent 5,500,449, March 19, 1996.

XIV.3. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons," U.S. Patent 5,504,118, April 2, 1996.

XIV.4. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons," U.S. Patent 5,506,272, April 9, 1996.

XIV.5. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons," U.S. Patent 5,543,437, August 6, 1996.

XIV.6. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons, U.S. Patent 5,620,670, April 15, 1997.

XIV.7. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons, U.S. Patent 5,621,155, April 15, 1997.

XIV.8. C. B. Benham, M. S. Bohn and D. L. Yakobson, "Process for the production of hydrocarbons, U.S. Patent 5,645,613, July 8, 1997.

XIV.9. H. C. Anderson, J. L. Wiley and A. Newell, "Bibliography of the Fischer-Tropsch Synthesis and Related Processes, Bureau of Mines Bulletin, 544, (1955).

XIV.10. C. N. Satterfield and G. A. Huff, Jr., "Carbon Number Distribution of Fischer-Tropsch Products Formed on an Iron Catalyst in a Slurry Reactor, J. Catal., 73, 187-197, (1983).

XIV.11. Baird, Schehl and Haynes, "Fischer-Tropsch Processes Investigated at the Pittsburgh Energy Technology Center Since 1944," Ind. Eng. Chem., Product. Res. Dev., 19, 175-191, (1980).

XIV.12. H. Pichler, "Twenty-Five Years of Synthesis of Gasoline by Catalytic Conversion of Carbon Monoxide and Hydrogen," Advan. Catal., 4, 272-341 (1952).

XIV.13. J. S. Swart, G. J. Czajkowski and R. E. Conset, "Sasol Upgrades Synfuels with Refining Technology," Oil & Gas J., August 31, 1991.

XIV.14. G. Weber, "Carthage Hydrocol Project," Oil & Gas J., 47 (47), 248-250, (1949).

XIV.15. A. P. Raje, J. Inga and B. H. Davis, "Fischer-Tropsch synthesis: process considerations based on performance of iron-based catalysts," Fuel, 76, 273 (1997).

XIV.16. L. Konig et al., "The Influence of Water and of Alkali Promotor on the Carbon Number Distribution of Fischer-Tropsch Products Formed over Iron Catalysts,", Ber. Bunsenges. Phys. Chem, 91, 116-121 (1987).

XIV.17. M. D. Schlesinger, J. H. Corwell, M. Leva and H. H. Storch, "Fischer-Tropsch Synthesis in Slurry Phase," Eng. and Process Dev., 43, 1474-1479, (1951).

XIV.18. C. B. Benham, "A decade of research and development in Fischer-Tropsch applications, Pittsburgh Coal Conf, October 15, 1992.

Table XIV.1			
	No. 1 Diesel ASTM (1)	No. 2 Diesel ASTM (2)	F/T Diesel
Cetane Index ASTM 976-80	45 min.	40 min.	62
Sulfur Wt.% ASTM D129-80 90% Distillation	.50 max	.50 max	<0.0001*
Temperature °F ASTM D56 Viscosity @ 40°C	550°F-max.	540°F-min. 640°F0Max.	556°F
cSt.	1.4 min.	1.9 min.	1.8
ASTM D445-82	2.5 max.	4.1 max.	
Conradson Carbon on 10%; ASTM D189-81 Wt.%	.15 max.	.35 max.	.02
Flash Point °F, min. Corrected to 760 mm Hg ASTM D56-82	100°F	125°F	122°F
Aromatic Content, Vol. %; ASTM D1319	8% min.	33%	less than 1%
API Gravity ASTM D1298	38-41	34.7	48.7
BTU/lb ASTM D240	16,000-17,000	19,810	19,371
Oxygen Content, Wt.%	N/A	N/A	3.05%
* Analyses were below limits of detection. (1) ASTM D975-81, #1 Diesel (2) ASTM D975-81, #2 Diesel			

Table XIV.2			
Test	Method		Results
Flash Point, ^{o}F	ASTM D56		122
API Gravity @ 60°F	ASTM D1298		48.7
Sulfur Content, Wt.%	Horiba Analyzer		<0.0001
Kinematic Viscosity @ 40°C, cSt.	ASTM D445-82		1.80
Distillation Range	ASTM D86	IBP 90% FBP	314 566 627
Conradson Carbon on 10% Residuum, Wt.%	ASTM D189-80		0.02
Saturates, Wt.% Alpha-Olefins Internal Olefins Alcohols and Others	NMR/90 MHz		30 45 9 16
Oxygen Content, Wt.%	Elemental Analysis		3.05
Average Carbon Chain Length	GC/FID		C_{14}
Cetane Index	ASTM D976		62
Heat of Combustion, BTU/lb	ASTM D240		19,371

Table XIV.3

Efficiencies Taken from Description of Examples
Feed 1,000,000 Std. Cubic Feet/Day

Example	Efficiency	C_{5+} bbl/day	CO_2 Recycle
1	58.1	80.7	
2	50		Yes, reactor and reformer
3	36.8	51.8	No
4	43.6	61.3	Yes, from reformer inlet
5	60.5%	85.2	Yes, reformer and 1/2 FT tail gas
6	71.3%	94.6	Yes, ~ all CO_2 and 1/2 FT tail gas hydrocarbons
7	43.7[a]	60.0	

a. Same as example 5 except a = 0.7.

Table XIV.4 Stream Compositions for Case III			
Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Town Gas (Vol. %)
H_2	55.7	56.32	56.15
CO	26.9	3.69	10.00
CO_2	2.0	17.88	13.56
CH_4	14.1	19.75	18.21
C_2H_6	1.3	2.05	1.84
C_2H_8	0.0	0.19	0.14
C_4H_{10}	0.0	0.12	0.09
LHV (B/ft.3)	388.3	387.1	387.4
Volume (MMSCF)	1.0	0.572	0.786

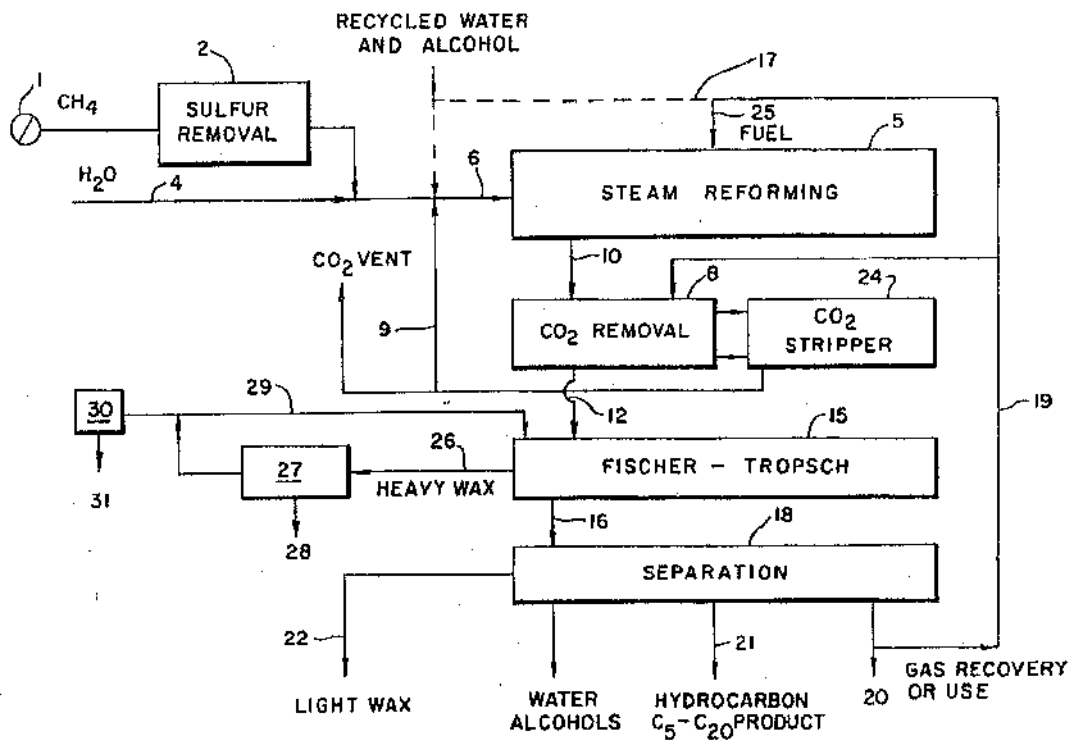| Species	From Gasifer (Vol. %)	From F.T. Reactor (Vol. %)	Mixed Gas (Vol. %)	Town Gas (Vol. %)
H_2	55.7	56.32	56.17	65.34
CO	26.9	3.69	8.59	10.00
CO_2	2.0	17.88	14.52	0.60
CH_4	14.1	19.75	18.57	21.57
C_2H_6	1.3	2.05	1.89	2.20
C_2H_8	0.0	0.19	0.16	0.18
C_4H_{10}	0.0	0.12	0.10	0.11
LHV (B/ft.3)	388.3	387.1	387.7	450.9
Volume (MMSCF)	1.0	0.572	0.773	0.664

Table XIV.5
Stream Compositions for Case IV

Figure XIV.1.   Recycled water and alcohol.