ATTACHMENT XII

Review of Fischer-Tropsch Work by Gulf Oil

The Gulf-Badger process leads from the catalysis research work on Fischer-Tropsch synthesis work and the reaction engineering analysis conducted by Gulf Oil, and later the process and engineering design provided by Badger (XII.1). A simplified process scheme is shown in Figure XII.1 (XII.2). The process was first discovered from exploratory work conducted by Gulf in the early 1970s. As Gulf continued to discover large reserves of natural gas, the need to convert remote natural gas to transportation fuels became important (XII.1). Since the exploratory research was successful, fundamental engineering and development work were undertaken, in the early 1980s. Because of its experience with others in the Fischer-Tropsch Synthesis, the Badger Company was invited to participate in some of the experimental work on reactor development and later provided the process engineering as well as the basis for the process economics (XII.2).

The initial involvement by Badger was because they had experience with fluid bed reactors and already had two of them set up in their lab. Gulf management wanted rapid development and did not want to delay to build their own reactors. Gulf researchers apparently advised against using the cobalt catalyst in a fluidized bed reactor but the work progressed to the point where 100 g batches of catalysts were prepared. The catalyst proved to be so active they had to strip insulation off the reactors when the reaction started to go out of control.

More money was spent on the fluid bed work in six months than Gulf had spent in the previous six years. With the result, of course, that the catalyst behaved just as Gulf researchers had predicted. The unit ran fine for half a day or so but then it began

to be difficult to keep the catalyst suspended. The catalyst had to be hydrogen-stripped once or twice a day, and the methane make was so high during those stripping periods that the overall selectivity to liquids was rather poor.

At the same time, the go-ahead for fixed bed development was given, and Gulf continued with Badger because they were already familiar with the catalyst and process. The scale-up of the fixed bed process of the catalyst manufacture by Davison were successfully accomplished.

Two types of reactors - two fluid-phase fixed bed and fluidized bed - were seriously considered. Because of the high molecular weight products that are produced by Gulf's most promising catalysts and thermal instability of the reactor, the fluidized bed reactor design concept presented real problems. Therefore, the Gulf Oil reaction engineering staff selected a fixed bed reactor. Its design and operation were critical, but success was quickly achieved.

The proprietary catalyst (in 1983) was inherently stable when combined with the proper reactor design and operation. Catalyst activity decay was avoided when stable, parametrically insensitive conditions and operation were achieved. The catalyst could be regenerated to the original activity by controlled oxidation and reduction.

The catalyst activity is an important property. It has a direct impact on the reactor design and operation as well as on capital and operating costs. The catalysts activity and selectivity in the developed reactor determine the reactor size that is required to produce a given quantity of desirable product, and to convert a given volume of synthesis gas, per day.

Operating conditions also influence the catalytic conversion and selectivity, and thereby the product distribution. An increase in temperature increases the reaction

rate whereas decreasing the H_2/CO ratio at constant temperature and pressure decreases the rate with the Gulf catalyst (XII.2). It was found that a 10°C increase in temperature would just about compensate the rate loss for a decrease in H_2/CO ratio from 2 to 1.5. A substantial increase in reaction rate results from increasing the total pressure. The results for increasing pressure and temperature are illustrated in Figures XII.2 and XII.3 (XII.2). Representative data are summarized in Table XII.1 (XII.2). The Gulf-Badger reactor design has a constrained range of performance and acceptable operation.

Production of C_5+ products depends upon both the activity and selectivity of the catalyst, and is a product of these two factors. Thus, some of the effects that increase activity may decrease productivity.

Pilot plant data for a reactor, consisting of a single, commercial-size reactor (1" x 40') tube show that reasonable temperature control can be achieved. Conditions that are representative of those used at Gulf are (XII.2):

Temperature . . . . 200-225°C

Pressure . . . . 250 psig

H_2/CO feed ratio 1.5-2

Feed space velocity . . . . 500-1,000/hr.

CO conversion . . . . 40-60% per pass

Selectivity to C_5+ . . . . ca. 70-75% of carbon converted

A typical product make from a reactor operating under such conditions are illustrated in Table XII.2.

Two reactor concepts were tested during the pilot plant work - a tubular fixed bed and a fluidized bed at Badger. The latter was not satisfactory. Details on only the

fixed bed reactor were given in reference XII.2. Gulf's pilot plant consisted of two reactor sections in series (Figure XII.4, ref. XII.2). After initial operation, temperature of the hot spot in the Gulf Oil reactor did not exceed that of the average temperature by more than 5°C. The illustrated CO conversions depended linearly upon temperature, as did the relative rate (Figures XII.5 and XII.6; ref. XII.2). The productivity of C_5+ hydrocarbons did not increase linearly with temperature due to the relative increased production of light (C_1 - C_4) gaseous products (Figure XII.7; ref. XII.2).

A demonstration unit was designed (in 1983) that would produce approximately 15 b/d of naphtha, 15 b/d of diesel fuel and 7 b/d of wax from 350,000 scf of natural gas (Figure XII.7; ref. XII.2). Natural gas was compressed to the reformer pressure and mixed with recycle CO_2, heated and passed through a zinc oxide bed to remove sulfur compounds. The natural gas was obtained by drilling a well at the laboratory site. It then entered a steam-methane reformer and was converted to synthesis gas. Carbon dioxide was removed in an amine scrubber after the gas was cooled and compressed. The gas then passed through a membrane separation system to adjust the H_2/CO ratio. Hydrogen would be used as fuel in the demo plant but could be utilized for upgrading in a commercial operation.

Gulf-Badger Process - Patent Literature

A series of catalysts was prepared that demonstrated a beneficial effect of a minor amount of ruthenium on a catalyst containing a major amount of cobalt for the low pressure synthesis of higher hydrocarbons from synthesis gas (XII.3).

A standard reference cobalt catalyst was prepared according to a published procedure (XII.4) whereby solution I (49.4 g. $Co(NO_3)_2 \cdot 6H_2O$; 11.0 g. $Mg(NO_3)_2 \cdot 6H_2O$ and 1.5 g. $Th(NO_3)_4 \cdot 4H_2O$ dissolved in 250 ml water) and solution II (35 g. K_2CO_3 in 250

ml water) were heated to boiling. Solution I was added rapidly with vigorous stirring to solution II, and immediately thereafter, 20 grams of dry powdered kieselguhr was admixed with stirring which continued for 10 minutes. The mixture was filtered and washed with distilled water until no evidence for nitrate ion was observed in the wash water. The solid was dried at 120°C for 16 hours, calcined in air at 350°C for 16 hours, then reduced in flowing hydrogen at 350°C for 3 hours. A second catalyst was prepared following the same procedure except that 0.35 g. of $RuCl_3$ was added to solution; this catalyst had the following composition: Co (31.6 wt.%); Mg (3.25 wt.%); ThO_2 (1.98 wt.%); Ru (0.53 wt.%); and kieselguhr (62.64 wt.%).

These two catalysts were subjected to synthesis runs using the same experimental conditions (H_2/CO = 2; upflow reactor with preheater for feed gas; atmospheric pressure; gas hourly space velocity based on the total amount of charge gas was 250; g.c. analysis). A series of experiments were conducted at various reaction temperatures with the CO conversion levels shown in Figure XII.9. It is seen that a measurable conversion is obtained only at a temperature of about 125°C or higher. On the other hand, the same catalyst except that it contains Ru, exhibits appreciable conversion at 50°C and maintains this superiority with increasing reaction temperature. The products from the runs at 220°C with the standard Co catalyst and the Ru containing catalyst were analyzed. The products from the standard catalyst exhibited an ASF distribution, with an alpha value of 0.85 (Figure XII.10). The products from the Ru containing catalyst exhibited a product distribution that contained significantly heavier hydrocarbons; the alpha value, based on the curve in Figure XII.10, was 0.98. Thus, the addition of Ru to the standard catalyst resulted in a significant increase in the catalytic activity as well as producing a significantly heavier products.

The data indicated that the presence of Ru essentially eliminated the production of methane and ethane (however, this conclusion is on a relative basis). In addition, the C_{9+} product from the standard catalyst contained 29% of olefinic product compared to 4% with the Ru containing catalyst. The gaseous products were found to contain about 15 volume percent CO_2 for the standard cobalt catalyst but only traces of this gas were obtained with the Ru containing catalyst. While it is not stated how the samples were collected, the low value for the C_{9-11} product fraction, relative to lower and higher carbon number products (Figure XII.10), suggests that the products consisted of gaseous and liquid fractions that were subsequently analyzed separately, resulting in loss of some C_{9-11} hydrocarbons.

Similar catalysts were prepared. For catalyst 3, about equal amounts of alumina and magnesia were added to replace kieselguhr in the above Ru containing catalyst (31.6 wt.% Co, 2.0 wt.% thoria, 0.5 wt.% Ru, 32.9 wt.% alumina and 32.9 wt.% magnesia). The other catalyst (4) contained a lower amount of Co and no thoria; at the same time alumina was substituted for the kieselguhr and the amount of magnesium oxide was increased. This catalyst (XII.4) contained 17.77 wt.% Co; 0.70 wt.% Ru, 40.77 wt. % alumina and 40.77 wt.% MgO.

The three catalysts were compared for methane production at various reaction temperatures; these results are compiled in Table XII.3. Referring to Table XII.3, it is apparent that the presence of Ru significantly decreased the amount of methane produced at all reaction temperatures. All Ru containing catalysts produced only traces of CO_2. Substituting gamma-alumina for kieselguhr had little, if any, effect on methane production; likewise, the removal of thoria and an increase in magnesia had little effect on methane production.

As shown in Table XII.4, it is noted that the "% selectivity for C_{9+} fraction" increased, and the % olefin in the fraction decreased, when Ru was present in the catalyst.

It appears that another Gulf worker later repeated Kobylinski's work with precipitated Co and CoRu catalysts, as well as one with the $20Co-0.5Ru-1La_2O_3$ composition. Ru was found to confer better dispersion and activity, just as it did for the impregnated catalysts, but that there was no appreciable change in product distribution in standard week-long tests. Apparently a problem with the GC analysis, such as getting drops of liquid product in with the vapor phase products impacted the reported data. The precipitated catalysts were found to have activities per unit weight of metal that were intermediate between those of catalysts made by aqueous impregnation and those made by nonaqueous impregnation.

High octane gasoline and diesel fuel are produced from synthesis in a two stage process (XII.5). In the first stage, synthesis gas is converted to straight chain paraffins that have a boiling range that falls mainly in the diesel fuel range. A cobalt catalyst, preferably containing a Group IIIB or IVB metal oxide, is supported on gamma- or eta-alumina, or a mixture of these two aluminas. The C_5-C_9 straight chain portion of the product from the first stage is converted in the second stage to highly aromatic plus branched chain paraffinic gasoline using a platinum group metal catalyst. The most preferred metal oxide for use in the catalyst for the first stage is thoria. The support should have low acidity, meaning a Brønsted acidity with H_o #1.5, which is less than 5 micromole per gram (about 10^{16} acid sites per m^2 of surface area). The deleterious effect of acidity is the isomerization and cracking of intermediate alkenes, removing them from chain growth and producing a low molecular weight product. **This latter**

statement implies that higher molecular weight alkenes readsorb on the catalyst to react with synthesis gas (or other alkenes) to produce higher alkenes. In addition, the production of low molecular weight products requires either that low molecular weight alkenes do not readsorb to undergo subsequent chain growth or that the low molecular weight products produced by cracking are alkanes, and not alkenes.

The catalyst for the first stage was defined by hydrogen chemisorption and should adsorb at 25°C from 125 to 300 micromole per gram of total catalyst. The chemisorption of hydrogen is illustrated in Figure XII.11 and shows a maximum for a catalyst that is receded in flowing hydrogen at 350°C. The maximum hydrogen adsorption corresponds to a dispersion, d, of cobalt of 0.066; that is, 6.6% of the Co atoms are located on the surface of cobalt metal crystallites.

The support must be of high purity and have a surface area in excess of 50 m^2/g, and preferably in the range of 150 to 225 m^2/g. High purity means that the support will contain negligible amounts of sodium, sulphate, silicon, phosphates or other material having a deleterious effect on the metal dispersion or the production of high molecular weight hydrocarbons.

The preparation of the catalyst was accomplished using a nonaqueous, organic impregnation solution containing the soluble cobalt and Group IIIB or IVB salts in order to achieve the necessary metal loading and distribution. The alumina was calcined in air prior to impregnation, preferably in 5h 400 to 600°C range. Suitable solvents include ketones, such as acetone or methyl ethyl ketone; the lower alcohols; amides, amines, ethers, hydrocarbons or mixtures thereof. A mixture of ethanol and acetone (4 parts

acetone; 1 part ethanol) is preferred and is used in an amount that will fill the pore volume; a maximum amount would be equivalent to five times the total pore volume.

The impregnated material is dried (25 to 45°C) to remove solvent to "dryness" and the material is then calcined in air, preferably 225 to 275°C. The impregnation, drying and calcination steps are repeated until the desired metal loading is obtained. The catalyst is slowly reduced in hydrogen. In the first reduction step, the catalyst is heated slowly (0.5 to 5°C/min) to a maximum temperature of 180 to 220°C and held at this temperature for about 24 hours. The second reduction step is accomplished by heating at a rate of 5 to 20°C per minute to the optimum temperature. Initially the reduction step is accomplished in a diluted hydrogen stream (e.g., 5% hydrogen in nitrogen); gradually the hydrogen concentration is increased to provide pure hydrogen.

While it is stated that the reactor type utilized is not critical, a fixed bed, with gas downflow, was preferred.

The catalyst for the second stage could be a typical naphtha reforming catalyst; that is, a platinum group metal supported on alumina using halogen to impart acidity.

The catalyst which gave the hydrogen adsorption data that is shown in Figure XII.11 contained the following composition by weight: 100Co/18ThO$_2$/200Al$_2$O$_3$. This catalyst was evaluated for activity using a flow of 240 cm^2/g/hr of CO and the same flow of H$_2$. Data were obtained for the above catalyst and are summarized in Tables XII.5 and XII.6.

The conversion depends upon temperature as is shown in Figure XII.12 (the numbers in parentheses are the total gas flow rate (cm^2/g/hr)). Thus, at a flow rate of 1:1 synthesis gas of 1.22 NL/g/hr; the conversion of CO was 6.5%. The activation energy was calculated using the data in Figure XII.12 to be 15 kcal/mole. The product

distribution changed slightly to favor lower weight products as the temperature increased (Figure XII.13). The product distribution did not adhere to the ASF plot except perhaps for the lowest temperature run; in all instances the C_2-C_4 products were much too low to approach fitting an ASF plot. It was not possible to fit the data in Table XII.2 with an ASF distribution.

This patent covers the activation of a promoted or unpromoted supported cobalt catalyst (XII.6). The catalyst is prepared using cobalt carbonyl and the support is either silica or alumina. The activation procedure comprises three steps: (1) reduction in hydrogen, (2) oxidation in an oxygen-containing gas, and (3) reduction in hydrogen, all three steps conducted at temperatures less than 500°C. This activation comprising reduction, oxidation and reduction has been called "ROR". It has been found that the addition of promoter, such as lanthanum or manganese (and oxides of the lanthanides and actinides), reduces the activity of the unpromoted catalyst. However, if in addition to the above promoters, ruthenium is also incorporated the ROR activation results in an increase in activity above that of the unpromoted cobalt catalyst.

The cobalt carbonyl is added by an impregnation technique using a non-aqueous solvent. If desired, the addition of promoter can be accomplished by co-impregnation along with cobalt. In the preferred procedure, the promoters (metal oxide and/or ruthenium) are added prior to the cobalt carbonyl.

Thus, the promoter is added to the calcined support as described in ref. XII.5. The impregnated catalyst, preferably using the incipient wetness technique, is dried slowly in air. The slow drying procedure is used so as to spread the metals over the entire support. After drying in air, the catalyst is calcined by heating slowly in flowing air to, preferably, 250 to 300°C. The drying and first calcination can be accomplished

separately, or done in a combined step. The calcination step is accomplished at a slow heating rate, preferably 0.5 to 1.0ºC/min., and held at the final temperature for up to 20 hours (2 h. is preferred). If necessary, the impregnation, drying and calcination steps are repeated to provide the optimum metals loading.

Following the calcination, the catalyst is impregnated with an organic solution containing cobalt carbonyl. Prior to impregnation, the catalyst is not exposed to the atmosphere sufficiently for the support to be rehydrated. If more than one impregnation is required, the catalyst must be subjected to a reduction-reoxidation treatment, the first two steps of the ROR procedure.

The preferred procedure for the ROR process is:

(1)   Slowly heat to about 200ºC and hold at this temperature for about 20 hours (starting with about 5% H_2 in nitrogen and increase gradually to pure H_2), then heat to the optimum reduction temperature (about 350ºC) and hold for about 24 h. Reduction should be slow enough to prevent the volatilization of cobalt carbonyl and to prevent the water vapor from exceeding 1% in the exit gas. Passivation is effected at room temperature using diluted air.

(2)   The oxidation step is conducted as described in ref. XII.5.

(3)   The oxidized catalyst is reduced as described in step (1) above.

The advantage of the ROR technique was illustrated by the preparation of three catalysts: (A) cobalt carbonyl was impregnated onto Ketjen gamma-alumina; (B) impregnating gamma alumina with cobalt and ruthenium nitrates (20 wt.% Co and 0.5 wt.% Ru); and (C) impregnating gamma-alumina with nitrate salts to give a material containing 25 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% lanthanum oxide. The three

catalysts were tested at 185°C; H_2/CO = 1.85 (atmospheric pressure), producing the results shown in Table XII.7.

The ROR treatment of the cobalt carbonyl catalyst provided a more active catalyst than the other two preparations and the selectivity of the cobalt carbonyl catalyst for C_5+ hydrocarbon is comparable to the ruthenium-promoted cobalt catalyst.

Hydrogen adsorption studies showed that the ROR treatment produced lower dispersions of Co than just hydrogen reduction. Thus, catalyst A had a metal dispersion of 0.29 following a reduction in hydrogen, but only 0.13 following the ROR treatment. Thus, the activity per metal site increased rather than the number of sites.

The activity of a silica-supported catalyst prepared using cobalt carbonyl is higher than that of an alumina-supported catalyst; however, the selectivity for C_5+ hydrocarbons is lower. The ROR treatment of the silica-supported material improves the C_5+ hydrocarbon selectivity.

This patent provides additional data to support the view that the reduction-oxidation-reduction, "ROR", technique provides superior activity over the same catalyst when it is just treated with hydrogen (XII.7). Data is also presented to show the improvement in activity when ruthenium is incorporated into the cobalt catalyst. The data shown in Table XII.8 was obtained at 1 atm pressure with [the patent gives the gas composition as weight percent but it surely is molar percent] a 35% CO and 65% H_2 synthesis gas mixture.

As shown in Table XII.8, the use or ruthenium significantly improved the catalyst activity as compared to the test of a catalyst that did not contain ruthenium. Even when the Co/Ru molar ratio exceeded 200/1, the catalyst activity increased in excess of 100 percent over that in which ruthenium was absent. Likewise, the ROR activation

led to a catalyst that exceeded the activity of a hydrogen treated material by 24-34 percent.

Data were also presented to show the benefit of Ru for a catalyst prepared by precipitation of cobalt, ruthenium and lanthanum oxide onto an alumina support by the addition of potassium carbonate. In this case the use of the ROR treatment improved the catalyst activity. However, when the amount of ruthenium exceeded 0.5 wt.%, the activity showed a decline of 4%.

A method of catalyst preparation is given which consists of an aqueous impregnation using a solution of a cobalt salt, drying the impregnated material and then employing a nonaqueous, organic impregnation solution of salts of ruthenium and a Group IIIB or IVB metal (XII.8).

A supported catalyst was prepared using a microspheroidal gamma-alumina commercially available from Harshaw; this alumina had an average particle diameter of about 60 microns. After calcination at 600°C, the alumina was impregnated with a cobalt nitrate solution. The material was dried at 120°C and then impregnated with thorium nitrate and ruthenium acetylacetonate dissolved in an acetone-ethanol (=2:1 ratio) solution. Excess solvent was removed at reduced pressure at room temperature in a rotary evaporator. The catalyst was then dried by heating to 90°C with the nitrate salt melting with evolution of water in the temperature range of 50-60°C. Prereduction and passivation was conducted using a hydrogen flow of 720 ml/g/hr. The catalyst was heated to 100°C at 1°C/min and maintained at this temperature for 1 hr and then heated at the same rate to 200°C. After holding at the latter temperature for 2 hr., the catalyst was heated at 10°C/min to 360°C and held at this temperature 16 hrs. After cooling below 200°C, the catalyst was flushed with nitrogen and the temperature

lowered to room temperature. Air was then bled into the nitrogen (1:50 air:nitrogen with flow of 50 mL per minute per 5 g catalyst for 16 hr). The final reduced catalyst contained 21.9 wt.% Co, 0.5 wt.% Ru, 2.2 wt.% Tho$_2$ and 75.4 wt.% alumina.

The activity of the catalyst was obtained using a 1/2" fluid bed reactor where 50 grams of catalyst was heated to a temperature of 350°C in a flow of hydrogen (N L/g/hr) and held at this temperature overnight. The hydrogen flow was reduced to 0.3-0.4 L/g/hr and an equal flow of CO was introduced (if H$_2$/CO = 2, the hydrogen flow was doubled). The results of runs are summarized in Table XII.9. The results show that, for similar conditions, an increase in the H$_2$/CO ratio from 1 to 2 caused a decrease in the C$_5$+ hydrocarbon yield and an increase in the amount of methane. An increase in pressure from 15 to 30 psia caused an even greater decrease in the C$_5$+ hydrocarbons and increase in methane; an increase in temperature had a similar effect.

A recent paper by Haddad and Goodwin (XII.16) on the CoRu catalyst claimed to obtain no change in activity from a ROR treatment. Looking at their catalyst preparation, they claimed to add 20% Co as the nitrate apparently in one step. This would appear to require the use of a supersaturated cobalt solution. In most catalysts, the alumina does not have enough pore volume to accommodate that much cobalt nitrate. The fact that they saw no ROR effect could be taken to mean that they had not produced an alloy catalyst whereas measurements of Curie point changes showed that the Gulf workers had done so. Goodwin reports TGA studies after a wide range of precalcination and reduction temperature, but none for an RO-treated catalyst. Gulf workers usually found a 100°C lowering in the reduction temperature for an RO-treated catalyst, compared to a fresh one - more evidence of a drastic change in properties.

The best proof of the advantage of ROR was obtained ona large scale - after one year of operation and several hydrogen strippings, the catalyst in the demo plant was regenerated (mainly for experience with recalcination). It was then 50% more active than it had been after initial startup and this made operation with the regenerated catalyst even more difficult. After the plant was shut down Gulf workers tested catalysts from about 20% of the reactor tubes and the catalysts, except for one tube, had the expected catalytic properties.

This patent relates to the use of a mixture of a catalyst active for the Fischer-Tropsch synthesis and one that effects alkene isomerization and/or cracking to produce gasoline from synthesis gas (XII.9). The Fischer-Tropsch synthesis catalyst is any one of the many examples that are comprised of cobalt alone or promoted by ruthenium and/or Group IIIB or IVB metal oxides. The acid cracking/isomerization catalyst is a silicalite-1 type (see XII.10 - XII.12).

An example utilized a catalyst containing 50 wt.% silicalite and 50 wt.% of a catalyst with the composition $100Co/18ThO_2/200Al_2O_3$ (example of conversion data given above). The particles were separately ground to give a particle size 100 mesh, mixed and then wetted, and then comminuting and sieving the resultant mixture to provide uniform 30-40 mesh particle size. Tests were conducted using 0.5 g samples of the prereduced catalyst by reducing in hydrogen at 360°C in hydrogen 2.4 L/g/hr at one atmosphere. The hydrogen flow was then reduced to 0.48 L/g/hr and an equal flow of CO ($H_2/CO = 1:1$). The tests were effected at 185°C and one atmosphere pressure to provide the data in Table XII.10.

The impact of the addition of silicalite to the Fischer-Tropsch catalyst is apparent (Figure XII.14). The ASF plot shows that alpha = ~1 for the C_3+ hydrocarbons; however

XII.15-Draft

the amount of methane is much above and the C_2 products much below the values expected for conformity to the ASF plot. When silicalite is added to the Fischer-Tropsch catalyst, the data do not fit the ASF distribution. Methane and the C_2-products are slightly higher than was obtained with the Fischer-Tropsch catalyst alone. More importantly, the C_3-C_{10} hydrocarbon products significantly deviate from the ASF distribution. Thus, it is apparent that the acid catalyst has effected a significant amount of isomerization and cracking of heavier hydrocarbons to lighter, gasoline range hydrocarbons.

The fraction of n-alkane in each carbon number hydrocarbon fraction provides a surprising distribution (Figure XII.15). When the catalyst contains only the Fischer-Tropsch component, the amount of n-alkane drops from about 75% for C_2 to about 20% for C_3 and then slowly increases with increasing carbon number to approach 60% for the C_{10} carbon number fraction. In this respect, the cobalt catalyst, when operated at 1 atmosphere, exhibits a distribution that is very similar to the one obtained for an iron catalyst at 1 atmosphere or at intermediate pressure levels (XII.13). However, when the silicalite catalyst is present, the alkane fraction deviates from the one obtained for Fischer-Tropsch synthesis. Up to carbon number 6, a similar trend is obtained for both catalysts; however, above carbon number 6 there is significantly less n-alkane when the silicalite is present. The apparent explanation for this is that the products have increasing fractions of isoalkanes, isoolefins and internal olefins as the carbon number increases above C_4, thus lower fractions of n-alkanes and 1-olefins. Isomerization to iso or internal olefins is not possible with C_2 and C_3. The degree of olefin reincorporation may be strongly influenced by the degree of substitution at the double bond. Ethylene readsorbs the most readily because it has two free CH_2 groups.

Among the 1-olefins, readsorption and chain initiation declines slowly with carbon number. Internal olefins readsorb poorly because they have no free CH_2 group, but they can isomerize back to 1-olefins and that gives them a small path towards readsorption. Isoolefins are also relatively unreactive. Although some have a free CH_2, if they have two substituents on the adjacent carbon that appears to be enough to make readsorption difficult.

All that is needed then to lower the effective chain growth probability among C4+ chains is for the 1-olefins, produced as primary products, to be isomerized to internal olefins or isoolefins. That removes them from the F-T reaction. With a catalyst that does this (almost any acidic catalyst), one can observe a large drop in chain growth probability between C_3 and C_4.

The isomerization to isoolefins requires a strong acid site and it was found that this reaction declined fairly quickly with time over silicalite or ZSM-5. However, the isomerization to internal olefins, which requires only moderate acidity, persisted for as long as any of the composites were run, and it was sufficient to alter the ASF distribution.

A layered aluminosilicate (montmorillonite-type structure) containing cobalt substituted into the crystal lattice was activated for the Fischer-Tropsch reaction using a sequential reduction-oxidation-reduction (ROR) technique (XII.14). A Group VIII noble metal, such as ruthenium, is also added by impregnation prior to the final reduction step.

The hydrothermally produced cobalt aluminosilicate has the following general formula prior to its activation:

$$Al_{4-n-x3}Co_{3/1n}O_8(OH,F)_4Si_{8-y}Al_yO(3x-y)NH_4^+zH_2O$$
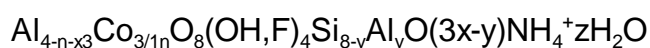
[it is 3x-+y in the patent]

where n is between 0.02 and 4 (prefer 2 to 3); x is up to about 1 (prefer 0.1 to 0.1); n+x between 0.02 and 4 (prefer 2 to 3); y is between 0.05 and 2 (prefer 0.5 to 2); and z is up to about 10. In the above the predominant amount of Al, Co, OH, and F are in the octahedral layers, and the Si and minor amounts of Al are in the tetrahedral layers. Ammonia and water are located between the layers. Water and ammonia are lost in the pre-activation calcination. The reduction is carried out in hydrogen (or other reducing gas) and the oxidation process is preferable accomplished in air or diluted air. The activation is accomplished in three steps - the ROR process described earlier.

A catalyst is prepared using a saturated aqueous solution of 161 g of $AlCl_3 \cdot 6H_2O$ in two liters of water that is slurried with 1.84 g of a silicic acid solution providing a Si/Al=4.7 ratio. The silica-alumina gel was precipitated by adding the slurry to 1 L of ammonium hydroxide with a pH of 8. The gel was washed with distilled water to remove chloride. A 50 g sample of the washed gel was slurried with 225 ml of water containing 60 g of cobalt acetate, 0.78 g of ammonium fluoride, and 0.42 g of HF while stirring and maintaining the pH at 8.-0 by adding ammonium hydroxide as needed. The mixture was heated at 300°C in an autoclave (1,240 psig) for four hours. After drying at 120°C, the gel was calcined at 500°C for 4 hrs and produced a hard, wine-red solid with $SiO_2/Al_2O_3 = 0.30$. The catalyst was reduced at 400°C for 2 hr in hydrogen and then reoxidized at 500°C. A hydrogen reduction at 600°C (16 hr.; 8.5% wt. loss) then reoxidized in air at 500°C (8.1% wt. gain). A final reduction was effected at 400°C for 16 hours.

This catalyst was utilized at 1 atm. in a 0.5 g. catalyst bed using a hydrogen:carbon monoxide = 1:1 with a feed of 0.48 l/g/hr. Three temperatures were utilized following activity stabilization to produce the results shown in Table XII.11. The major products in the C_5+ hydrocarbons were found to be isoalkanes and isoalkenes. The alkenes contained a high fraction of internal alkenes.

The catalyst is a rare earth promoted layered complex metal silicate composition characterized as having repeating units with a structural formula

$$[(1-x)Ni^a + xRu^b]_n(OH)_4Si_2O_5 \bullet wH_2O$$
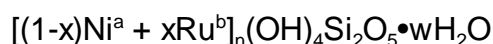
where x is a number from 0 to 1 (fraction of Ru in Ru+Ni); a is the valence of nickel, b is the valence of ruthenium; n is a number defined by

$$6/[a(1-x) + bx]$$

and w is a number ranging from 0 to 4 (XII.15). The preferred catalyst is a rare earth promoted nickel chrysotile.

These catalysts produce much methane in addition to higher carbon number hydrocarbons. Typical examples, using $H_2/CO = 2.5$; 350 GHSV; 210°C; and atmospheric pressure, are shown in Table XII.12.
Low concentrations of thoria are needed but higher (30% or more) are not beneficial, and may have a slight detrimental effect. The inclusion of low concentrations of thoria greatly increase the amount of C_2+.

Typical examples, using $H_2/CO = 2.3$; 400 GHSV; 204°C; and atmospheric pressure, to define the differences in rare earth promoters, if any, are shown in Table XII.13.
The results show that there is a synergistic benefit in conversion when a mixture of two rare earth promoters are used. Thus, thoria incorporation provides a CO conversion of

31.5% and lanthana 25%; rather than the expected intermediate value for CO conversion when a mixture of thoria and lanthana are incorporated, the CO conversion is 71.5%. A similar result is obtained when thoria and praseodymium is utilized.

Slurry Phase Synthesis

A patent (XII.17) claimed a process for the conversion of synthesis gas using a finely divided catalyst (ca. 10-110 microns) dispersed in a fluid medium. The catalyst consisted essentially of cobalt and ruthenium on a support. In subsequent claims the support was identified as alumina or silica. Another subclaim indicated that the fluid is a liquid medium which could be a synthetic hydrocarbon liquid or a hydrocarbon conversion product. The activation known as ROR (reduction in hydrogen, oxidation, reduction in hydrogen) was claimed. A promoter could be selected from the group consisting of Rh, Pt, Pd, Ir, Os, Ag and Au. The use of these catalysts produced a product with less than 16 wt.% methane. The catalyst cobalt concentration covered was from about 5 to about 25 wt.% and the promoter in an amount from about 0.01 to 0.5 wt.% based upon the total catalyst weight.

The patent contains examples of conversions in fixed-bed reactors with a catalyst prepared to have various particle sizes. A catalyst was prepared that had a particle size that one normally encounters in fixed-bed operations (1/16th inch (0.16 cm) extrudate) and then this catalyst was ground to produce average particle sizes of 0.28 and 0.54 mm. The found that both catalyst activity and product selectivity changed with particle size. In particular, the fraction of methane decreased and the amount of C_5+ increased with decreasing particle size of the catalyst (Figures XII.16 and XII.17); over the particle sizes tested it appears that both selectivities change linearly with particle size. It appears that the methane production of the three catalyst

sizes extrapolates to a common value of about 4 wt% at very small particle size (Figure XII.16). Likewise, the C_5+ selectivity appears to approach about 87 wt.% at very small particle size. This means that the C_2-C_4 yield is about 9 wt.% for the very small particle size catalyst. As expected, the rate of reaction increased as the particle size was decreased (Figure XII.18). For the smallest particle size (0.24 mm) the reaction rate increased by a factor of 1.94 for an increase in temperature of 10.5^{o}C, a factor close to the rule of thumb of a doubling in reaction rate for every 10°C increase in temperature. At 195°C, the rate decreased by 27% when the H_2/CO ratio was decreased from 2.0 to 1.5.

The authors indicate that the catalyst prepared using an organic solvent has higher activity than one prepared in the same manner but using an aqueous solution. The authors indicate that the catalyst may contain Group IIIB or IVB metal oxide as a promoter, with oxides of the actinide and lanthanide series being preferred. Especially preferred metal oxides are La_2O_3, CeO_2, ZrO_2, TiO_2, HfO_2, or ThO_2. MnO_2 and MgO are also listed as preferred promoters. The amounts of these promoters can be from about 0.05 to 100 parts by weight to 100 parts by weight of cobalt. It appears that the patent covers only catalysts using these oxides as promoters, and not as the support material.

The support should have low acidity. Its surface area should be at least about 40 to 50 m^2/g but not so high that "permit reactant materials to enter the interstices of the catalyst." A preferred surface area is in the range of 150 to 225 m^2/g. The support should be high purity, meaning having low concentrations of components having deleterious effects on the cobalt catalyst.

The process is outlined in figure XII.19 and does not differ significantly from one used by Kölbel and coworkers (XII.18). In the reactor, the catalyst particles are

suspended in a liquid medium having sufficient viscosity to ensure that the particles remain in suspension and having a volatility that is low enough to avoid loss due to vaporization within the reactor. The catalyst is present from about 2 to 40 wt.%. The catalyst density can be in the range of 0.25 to 0.90. The gas flow enters at a rate sufficient to suspend all of the catalyst particles in the system without settling. The gas flow rate will be selected depending upon the slurry concentration, catalyst density, suspending medium density and viscosity, and particular particle size utilized. Suitable gas flow rates include, for example, from about 2 to 40, preferably from about 6 to 10 cm/sec. The pressure range covered is from about 1 to 70 atm. Light hydrocarbon products, such as C_{20} and below, are withdrawn overhead through a line designated 32 in Figure XII.19. A portion of the heavier products and catalyst slurry is withdrawn through line 38 and is passed to a separation zone. A concentrated catalyst/slurry fraction is returned to the reactor while a portion of the catalyst/slurry may be passed through a regeneration zone (54) before being returned to the reactor. Heavy products with low catalyst concentration are revolved through line 44. Separation by filtration can be utilized for separating catalyst from the suspending liquid (vessel 40).

The data obtained in the slurry reactor were compared to a run in the fixed bed reactor with the same catalyst formulation. The catalyst for the fixed bed reactor was supported on 1/16 inch extrudate alumina which contained about 20 wt.% Co, 0.5 wt.% Ru and 1.0 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3, 24 wt.% Nd_2O_3, 0.7 wt.% CeO_2, 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides. The synthesis gas (H_2/CO = 2.03:1 with methane diluent of 19.1 mole %) passed through the 1" i.d. reactor at a maximum stable temperature of 215°C with a pressure of 275 psi (18.7 atm., 1895 kPa). For the slurry reactor, alumina which contained about 12 wt.%

Co, 0.3 wt.% Ru and 0.6 wt.% of a rare earth oxide composite containing 66 wt.% La_2O_3, 24 wt.% Nd_2O_3, 0.7 wt.% CeO_2, 8.2 wt.% PrO_2 and 1.1 wt.% other rare earth oxides was in the form of 20-105 microns (less than 140 mesh; average particle size 52 microns). A liquid with a viscosity of 8 centistokes (8×10^{-6} m^2/s) was composed mainly of C_{40}-C_{50} isoparaffins. Gas entered at the bottom through a stainless steel screen in the form of small bubbles. Hydrocarbon was removed from the top through a heated line. The pressure was 160 psig (10.7 atm) and the gas flow with H_2/CO = 1.95 was 1826 cm/s. Initially the temperature was 225°C but was increased and held at several higher temperatures to obtain additional conversion data.

The increase in conversion with increasing temperature gives an activation energy of 20.5 kcal/mol (85.7 kJ/mol) (Figure XII.20). This value of the activation energy is surprisingly close to that reported for a fused iron catalyst (20.0 kcal/mol; 83.6 kJ/mol) and a precipitated iron catalyst (20.9 kcal/mol;87.4 kJ/mol) (XII.19). At 225°C, methane is 8.4 wt.% of the product and increases to 15.6 wt.% at 240°C. As the temperature increases, the C_5+ fraction gradually decreases (Figure XII.21) and the C_5-C_{20} fraction increases, indicating that the alpha value decreases with increasing temperature; however, there is not sufficient data to obtain reliable values of alpha (Table XII.14).

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XII.6.   U.S. Patent 4,605,679; August 12, 1986; T. P. Kobylinski, C. L. Kibby, R. B. Pannell and E. L. Eddy.

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				Table XII.1		
			Evaluation of G-B Catalyst in Pilot Fluid Bed Reactor			
			Data Taken at 25 Hours on Stream (from XII.2)			
Run	Temp., ^{o}C	Pressure, (psig)	H_2/CO	Syngas Space Velocity, cm^3/g/h	Per Pass CO Conversion, %	Selectivity to C_5+[a]
First	195	15	2.0	600	25	74
Second	195	30	2.0	1200	22	82
Third	195	30	2.0	1200	16	74
	215	30	2.0	1200	44	71
Fourth	215	60	2.0	1950	41	72
Fifth	205	30	1.5	1200	17	72
Sixth	215	30	3.0	1200	76	55
Seventh	205	30	2.0	1200	23	67
Eighth	205	30	2.0	1800	25	73
Ninth	215	40	1.5	1600	25	72

a. C_5+ expressed as percent of carbon selectivity basis.
b. At some point, every run had one or more reactor "run aways." They all failed.

Table XII.2	
Typical Data from Fixed Bed Pilot Plant (XII.2)	
Temperature, ^{o}C	210
Yields, Wt.% of Hydrocarbon Product	
CH_4	13.7
C_2H_4 to C_4H_{10}	11.6
C_5-C_8 (naphtha)	25.4
C_9-C_{20} (distillate)	33.4
C_{21}+ (wax)	14.2
Oxygenates	1.7

		% Selectivity to CH_4 Catalyst from Example			
		Table XII.3			
		Influence of Ru on Catalyst Performance (from ref. XII.3)			
Experimental Conditions:		H_2:CO = 2:1, GHSV = 380			
Ex. No.	Temp., ℃	1 (Co)	2 (Co + Ru)	3 (Co + Ru)	4 (Co + Ru)
18	200	9.8	0[a]	0	0
19	300	27.5	0	0	0
20	400	48.0	0	1.2	0.5
21	450	87.0	10.1	21.0	25.0
a. The low selectivities (zero) are most likely not real.					

Table XII.4

Influence of Ru on the Production of C_9^+ (from ref. XII.3)

		% Selectivity to C_9+ Fraction Catalyst from Example Number in Table XII.3				% Olefins in C_9+ Fraction Catalyst from Example Number in Table XII.3			
No.	Temp., ℃	1	2	3	4	1	2	3	4
22	200	41	88	87	--	29	4	5	3
23	300	30	75	71	73	32	10	9	7
24	400	18	41	38	34	48	30	26	21

Table XII.5					
Products Using a Prereduced Co-Th-Alumina Catalyst (from ref. XII.5)					
Example No.	2	3	4	5^2	6^3
Temp., $^{\circ}$C	175	185	195	205	194
H_2/CO	1:1	1:1	1:1	1:1	2:1
CO Flowrate (cm^3/gram/hour)	155	155	270	610	270
CO Conversion Rate (cm^3/gram/hour)					
To CO_2	0.2	1.1	1.6	2.9	(1.3)
To Hydrocarbons	19	41	61	79	(120)
CO Conversion (Percent)	13	27	23	13	44
Product Distribution (Carbon Atom %)					
CH_4	4	5	6	8	9
C_2-C_4	6	7	8	10	9
C_5-C_8	23	25	29	34	24
C_9-C_{20}	62	59	50	44	49
C_{21}+	5	4	7	4	9

2. Separate run.
3. Not aged at 205°C.

Table XII.6	
Alpha Values for Runs Shown in Table XII.5 (From ref. XII.5)	
Run Number	Alpha, Based on C_5-C_8/C_9-C_{20}
2	0.89
3	0.82
4	0.83
5	0.79
6	0.74

Table XII.7				
Impact of ROR (reduction-oxidation-rereduction) of a Co Catalyst (from ref. XII.6)				
	CO Conversion Rate (cc/gram Co/hour)		C_5+ Liquid (Wt.%)	
Catalyst	R350	ROR	R350	ROR
A	1230	1485	73	81
B	790	1190	80	79
C	690	960	81	--

Table XII.8					
Influence of Ru on Activity of a Co Catalyst (from ref. XII.7)					
		Co/Ru Ratio		195°C CO Conversion Rate (cc/gram metal/hour)	
Test No.	Ru (Wt.%)	(Wt.)	(Molar)	R350 (F)	ROR (G)
1	0.0	---	---	382	476
2	0.05	400	693	780	968
3	0.10	200	346	879	1093
4	0.50	40	69	1034	1415
5	1.00	20	35	930	1286

Table XII.9 Influence of Temperature on a Co-Th-Alumina Catalyst (from ref. XII.8)					
Example No.	2	3	4	5	6
Temp., $^{\circ}$C	195	195	195	205	215
Pressure, psia	15	15	30	30	30
H_2/CO	1:1	2:1	2:1	2:1	2:1
CO Flowrate (cm^3/gram/hour)	310	310	735	735	735
CO Specific Rate (cm^3/gram/hour)	70	95	102	200	257
C_5+ Synthesis Rate (mg/gram/hour)	38	48	47	83	97
Product Distribution Carbon (Atom %)					
CH_4	6	10	15	19	22
C_5+	88	79	73	64	58
C_9-C_{20}	57	45	41	32	25
C_{21}+	9	5	6	4	1
CO_2	2	2	1	2	2

Table XII.10 Influence of Silicalite on the Product Distribution (from ref. XII.9)				
	$Co/ThO_2/Al_2O_3$		$Co/ThO_2/Al_2O_3$ + Silicalite	
Carbon No.	Carbon Atom %	Wt.% n-Paraffin in Fraction	Carbon Atom %	Wt.% n-Paraffin in Fraction
1	4.7	(100)	11.3	(100)
2	0.7	50	1.8	75
3	2.5	15	8.4	24
4	3.5	20	23.2	25
5	5.0	25	23.1	35
6	6.1	33	14.9	45
7	6.8	46	9.0	38
8	7.5	56	4.8	22
9	8.5	58	2.3	13
10	9.4	62	0.9	5
11+	45		1	

Table XII.11			
Products from the Conversion of Syngas with a Co-Silica-Alumina Catalyst (from ref. XII.14)			
	Temperature, °C		
	175	185	195
Yield, Wt.%			
C_1-C_4	22	25	34
C_5-C_{11}	54	60	57
C_{12}+	24	15	9
Relative Rate, mg/g/hr[a]			
C_1-C_4	0.3	0.5	1.1
C_5-C_{11}	0.7	1.2	1.8
C_{12}+	0.3	0.3	0.3

a. The units or the numerical values are probably in error. They may be specific rates (mg/g cat/hr) but if this is the case, the magnitude of the values are questionable. In any event, it appears that the rates are only about one-tenth that of a good Co-Al_2O_3 catalyst. The low activity may be due to the difficulty of reducing Co in the above catalysts.

Table XII.12				
Effect of Thoria Concentration on Product Composition (from ref. XII.15)				
			Mol % Selectivity to	
Example No.	Wt.% ThO_2	% CO Conversion	CH_4	C_{2+}
30	0.5	31.1	92.0	8.0
31	1.5	29.0	55.0	45.0
32	2.0	30.5	57.0	43.0
33	3.0	33.2	57.5	42.5
34	5.0	31.0	54.3	45.7
35	10.0	28.6	55.5	44.5
36	20.0	21.4	58.2	41.8
37	30.0	11.2	50.3	49.7

Table XII.13

Relation of Catalyst Composition to Conversion and Product Selectivity (from ref. XII.15)

Example No.	Catalyst	Wt.% Rare Earth	% CO Conversion	% Selectivity to C_{2+}
11	Ni-Chrysotile	0	17.0	0
38	Th-Ni Chrysotile	2	31.5	43.0
39	La-Ni Chrysotile	2	25.0	39.0
40	Ce-Ni Chrysotile	2.5	32.5	32.1
41	Pr-Ni Chrysotile	2	35.3	35.0
42	Th + La-Ni Chrysotile	2 + 2	71.5	49.0
43	Th + Pr-Ni Chrysotile	2 + 2	69.1	48.0

Table XII.14

Conversion Data for Syngas Conversion Using Fixed-Bed and Slurry Reactors (from ref. XII.17)

Test Number	1	2	3	4	5
Reactor Type	fixed-bed	slurry	slurry	slurry	slurry
Temperature, ^{o}C	215	225	230	235	240
CO Conversion rate (ccCO/g/h)	215	649	808	992	1210
CO Conversion, %	45.3	8.4	10.4	12.8	15.6
Product Yields, Methane, wt. %	26.6	10.5	11.5	12.5	14.0
C_5-C_{20} (mg/g/h)	67	325	400	478	560
C_5+, wt.%	60.0	79.0	78.0	76.0	73.0
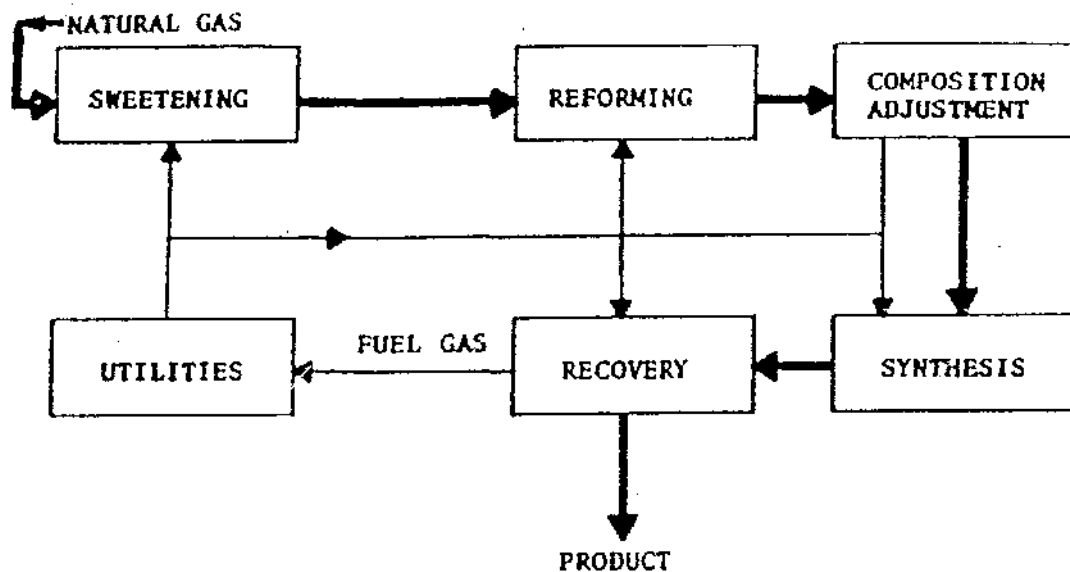
Figure XII.1.   G.B. process, remote natural-gas conversion (from ref. XII.2).
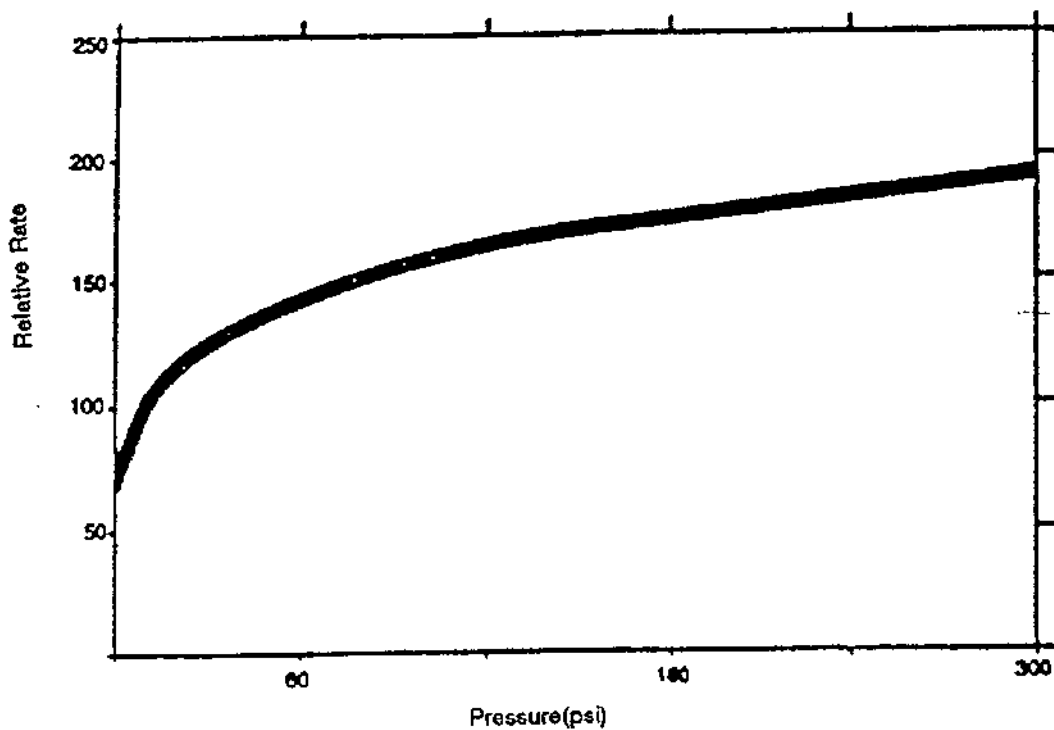
Figure XII.2.   Effect of pressure on catalyst activity (relative rate based on data as given in Table XII.1) (from ref. XII.2).
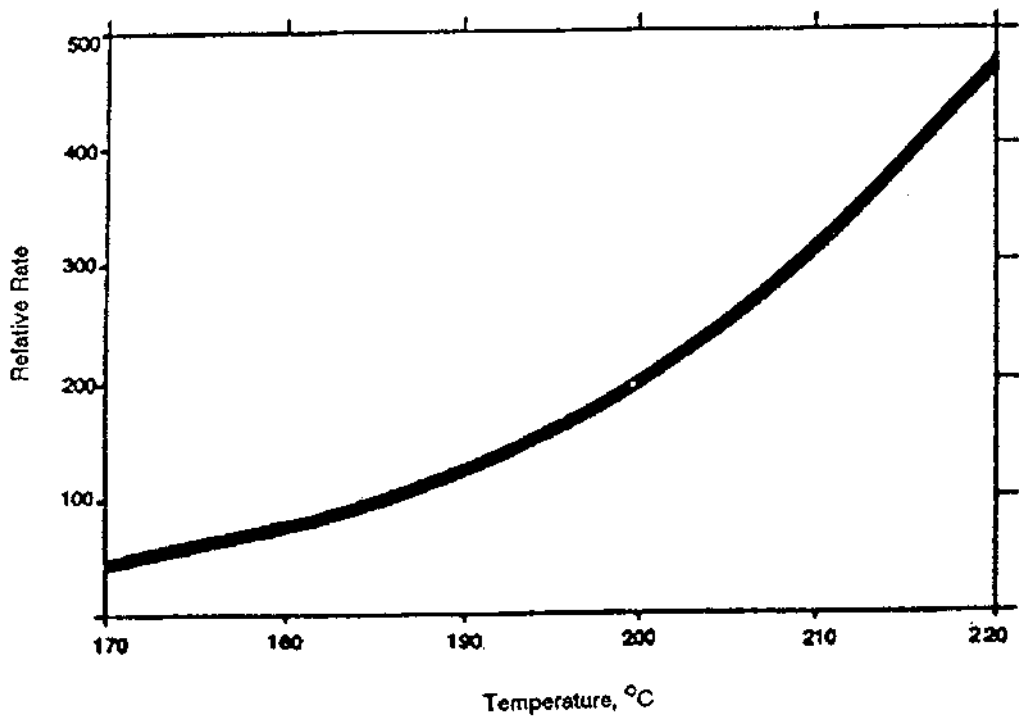
Figure XII.3.   Effect of temperature on catalyst activity (relative rate) (from ref. XII.2).

XII.34-Draft
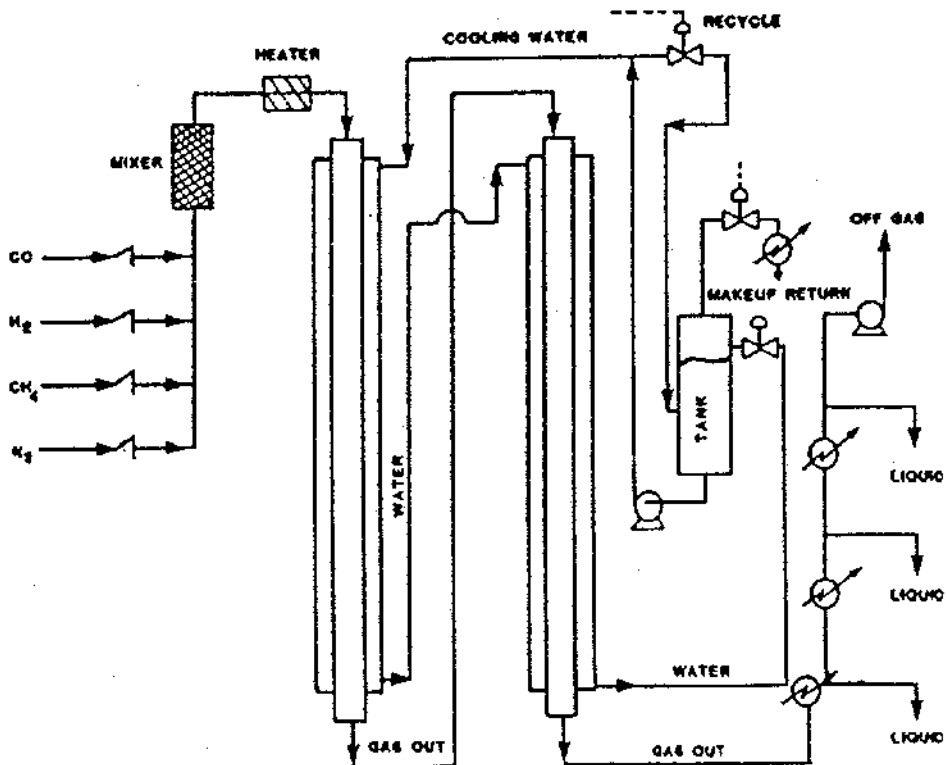
Figure XII.4.　　Schematic diagram of the pilot plant remote-gas-to-diesel fixed-bed process (from ref. XII.2).
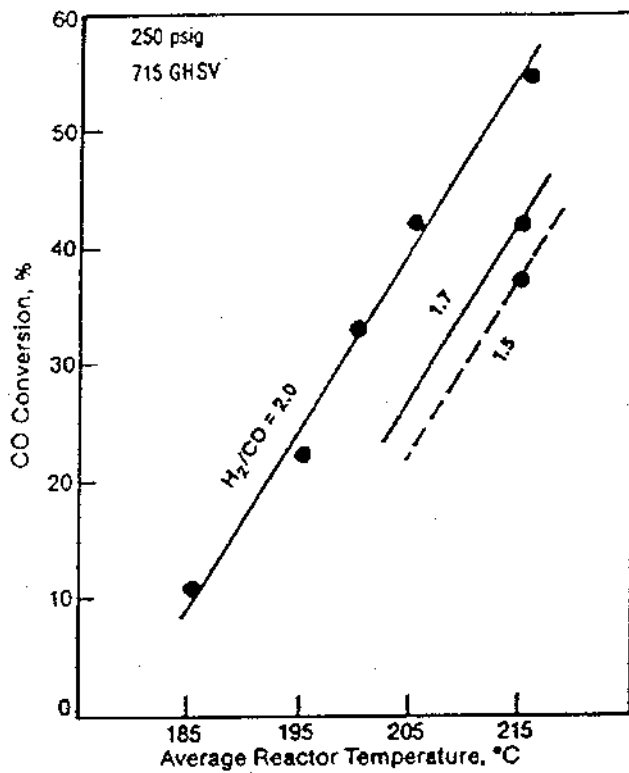
Figure XII.5.   Effect of temperature and H_2/CO on carbon monoxide conversion (from ref. XII.2).
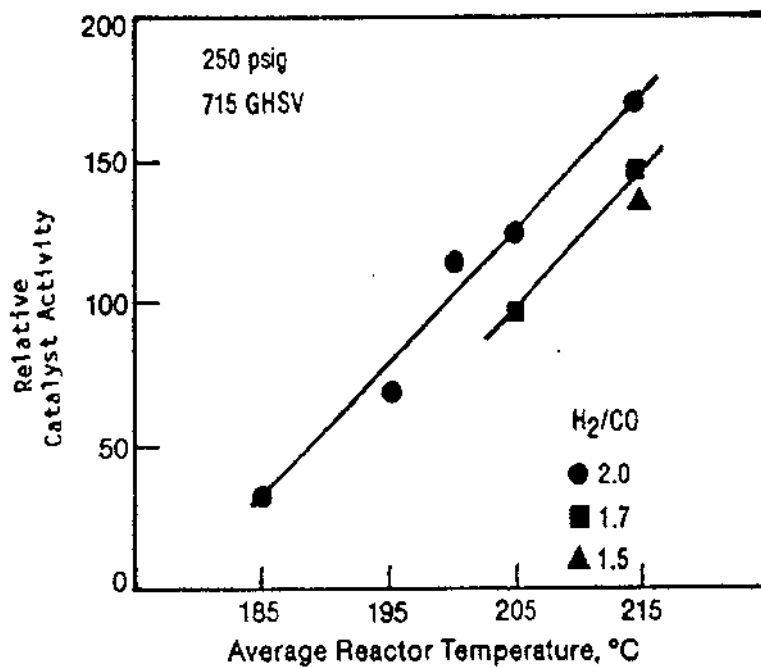
Figure XII.6.   Catalyst activity (from ref. XII.2).
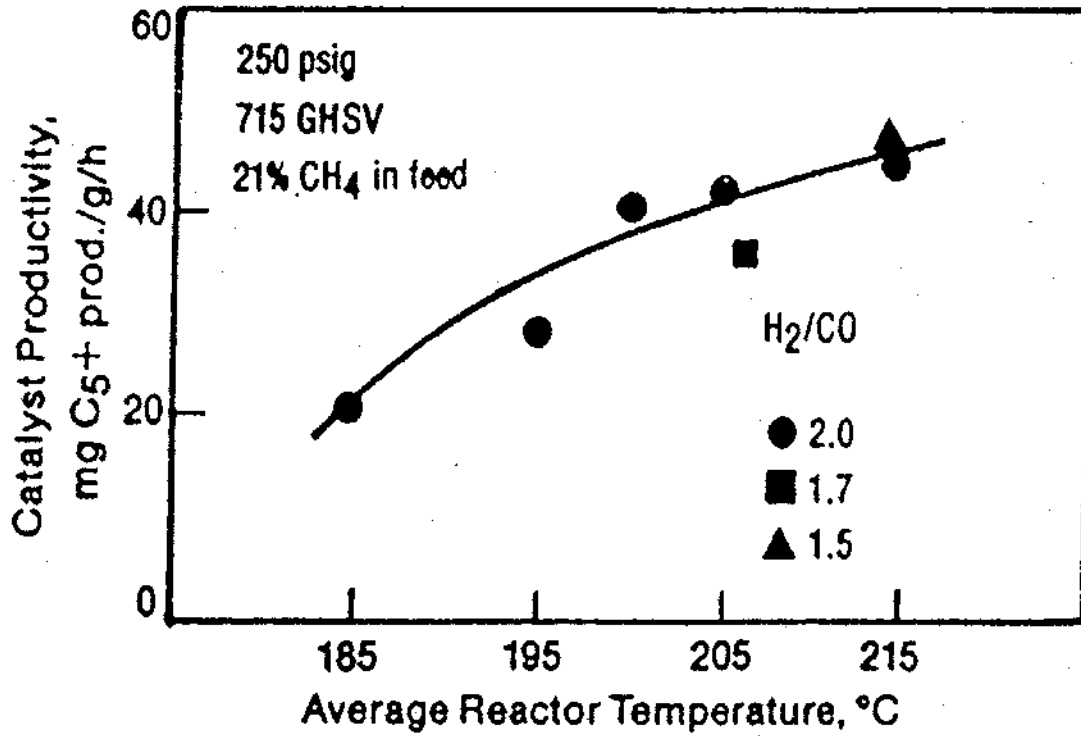
Figure XII.7.　　Catalyst productivity (specific rate) (from ref. XII.2).
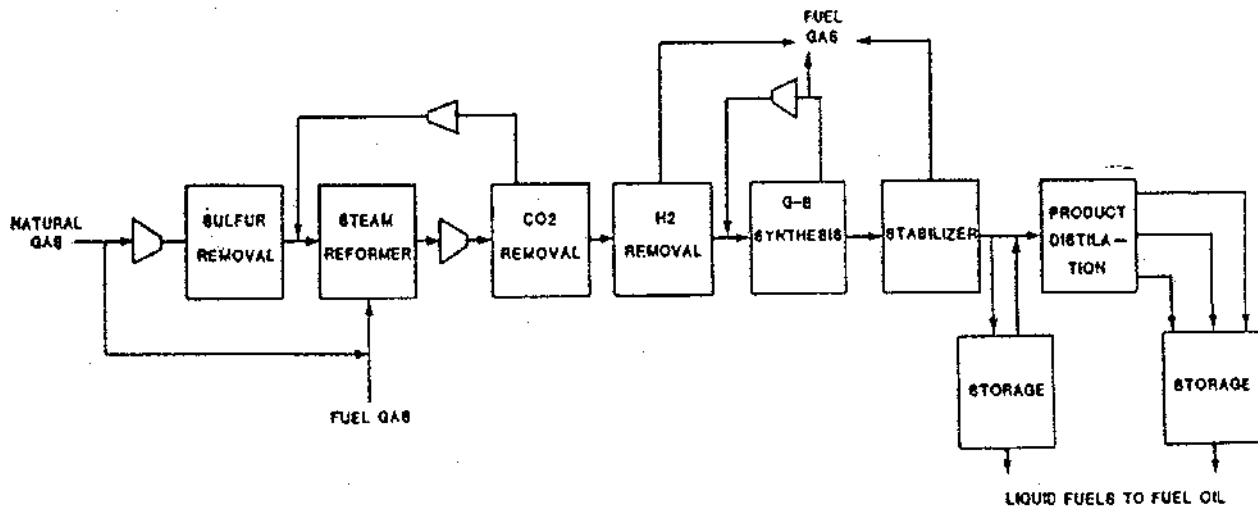
Figure XII.8.　　G.B. demonstration plant, block-flow diagram (from ref. XII.2).
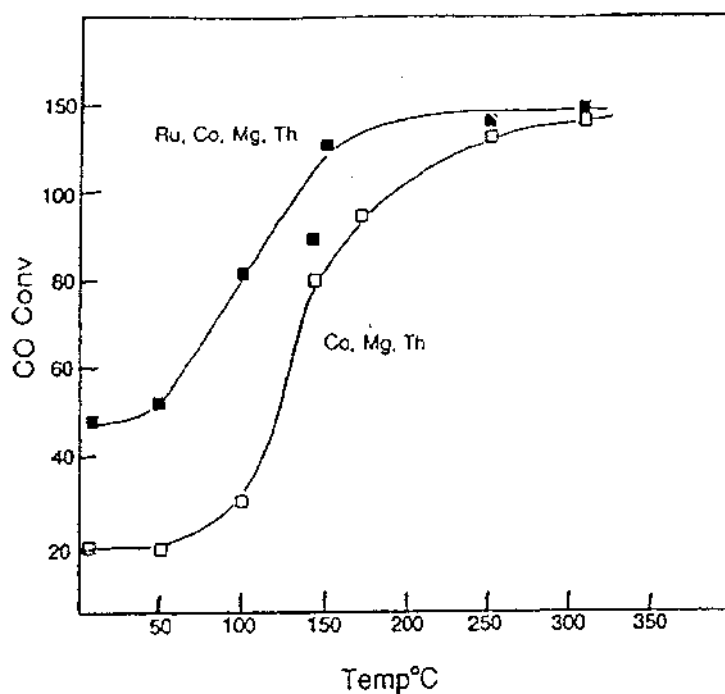
Figure XII.9.   The impact of Ru (# data points) on a Co (MgThO$_x$) catalytic
conversion as a function of temperature (data from XII.3).
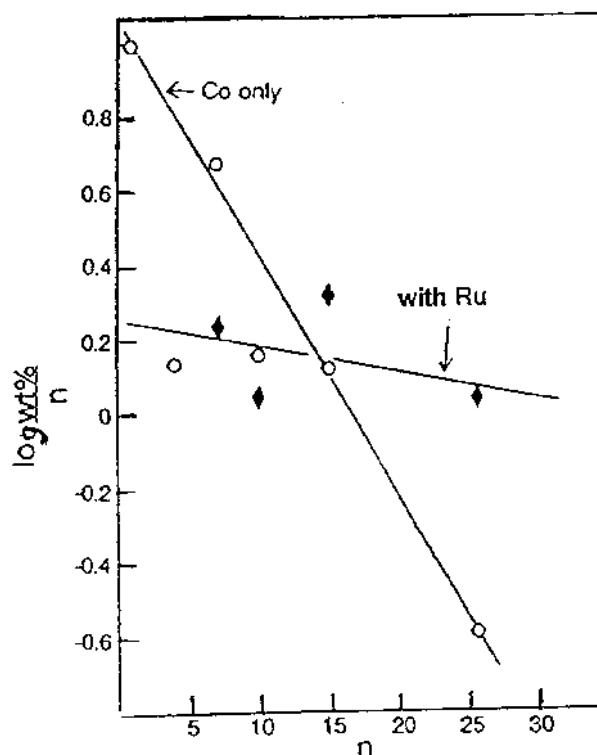
Figure XII.10.   Anderson-Schulz-Flory plot of the products from the synthesis using a
Co catalyst and one also containing Ru, Mg and Th) (data from XII.3).
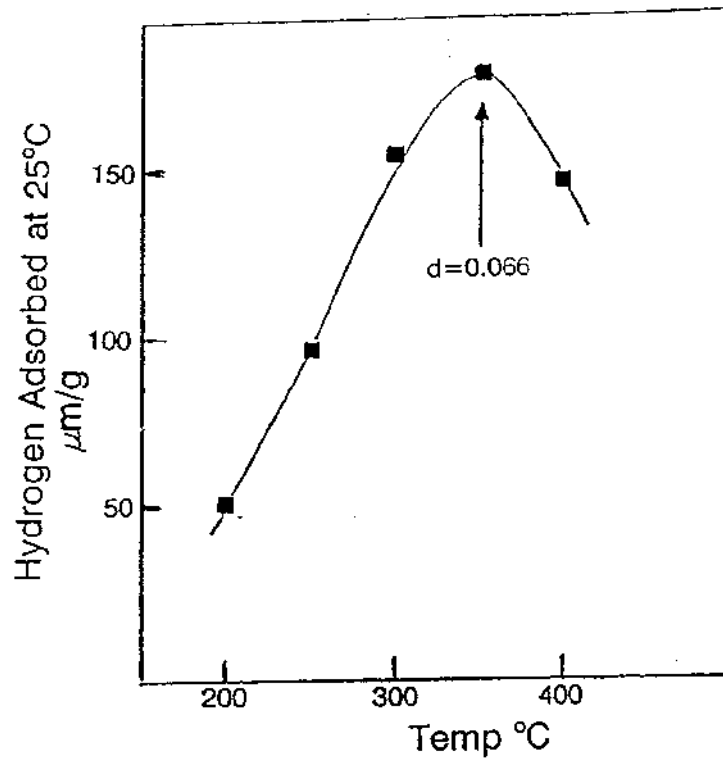
Figure XII.11.   Co dispersion measurements as a function of temperature (data from XII.5).
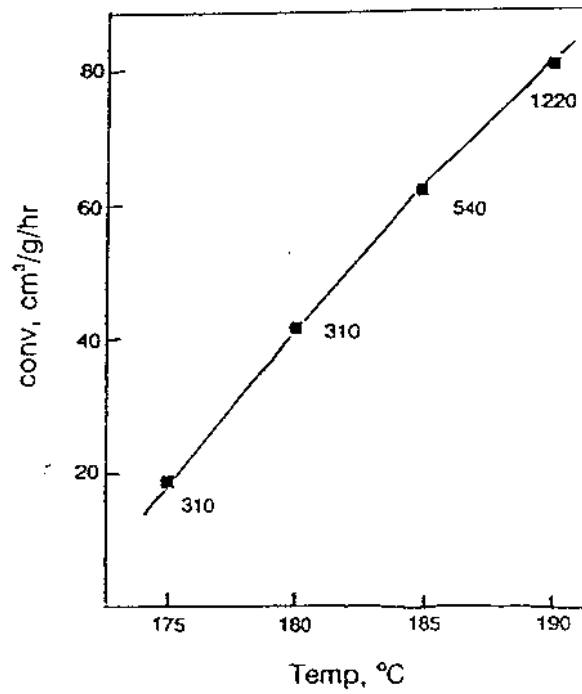
igure XII.12.   Dependence of CO conversion on the temperature (numbers in figure are the GHSV) (data from ref. XII.5).
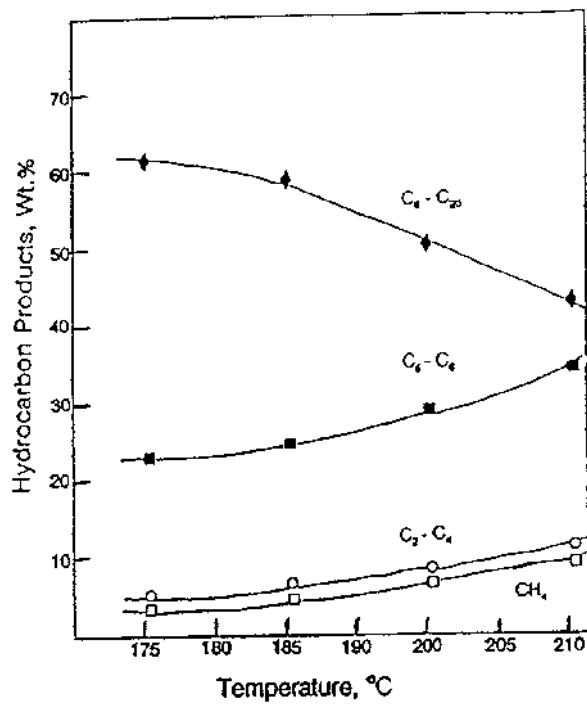
Figure XII.13.   Hydrocarbon product distribution for a cobalt catalyst as a function of temperature (data from XII.5).
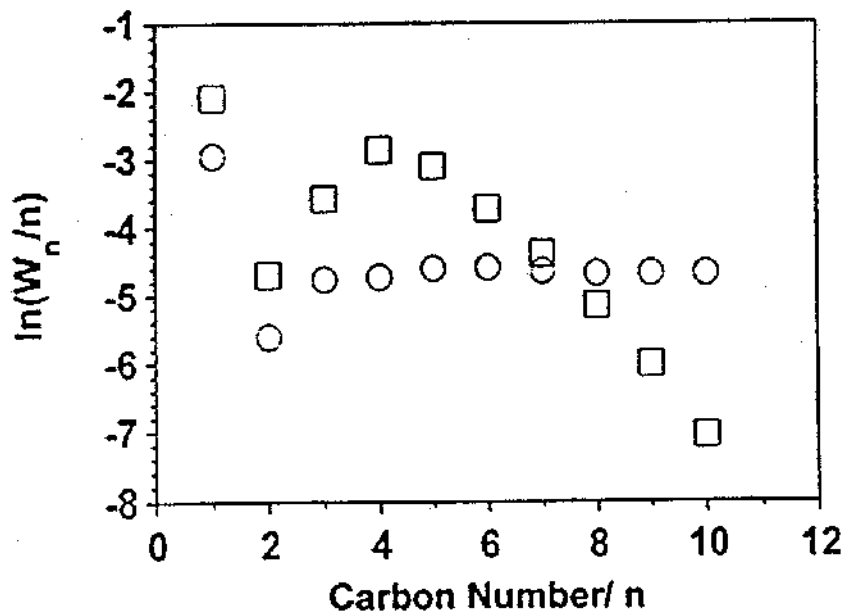
Figure XII.14.   Anderson-Schulz-Flory plot of the products from the Fischer-Tropsch synthesis with a cobalt (Th, Al_2O_3) catalyst alone (**F**) and physically admixed with a silicate zeolite catalyst (**G**) (data from XII.9).
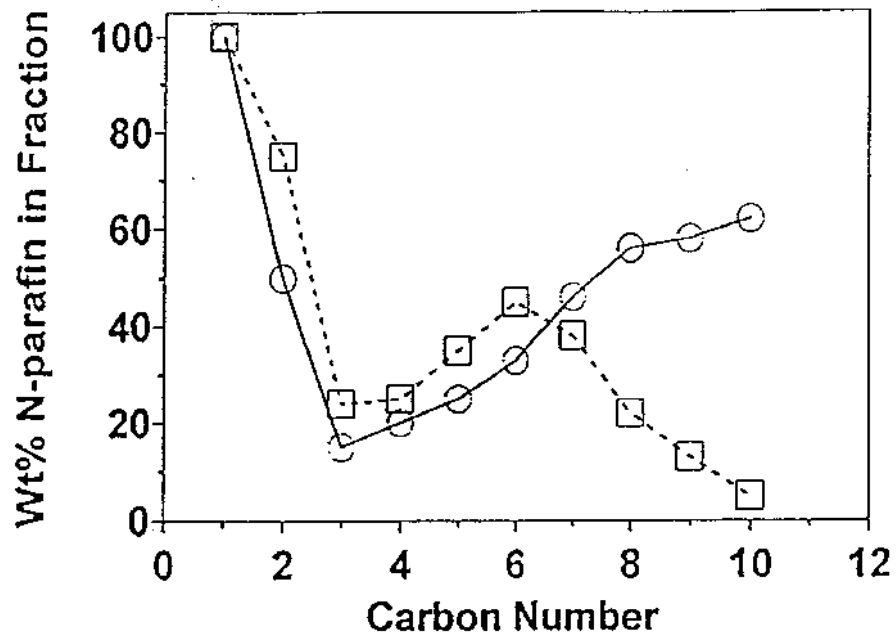
Figure XII.15.   Wt% N-alkane in the carbon fractions of the products from Fischer-Tropsch synthesis with cobalt (Th, Al_2O_3) catalyst (**F**) and physically admixed with silicate zeolite (**G**) (data from XII.9).
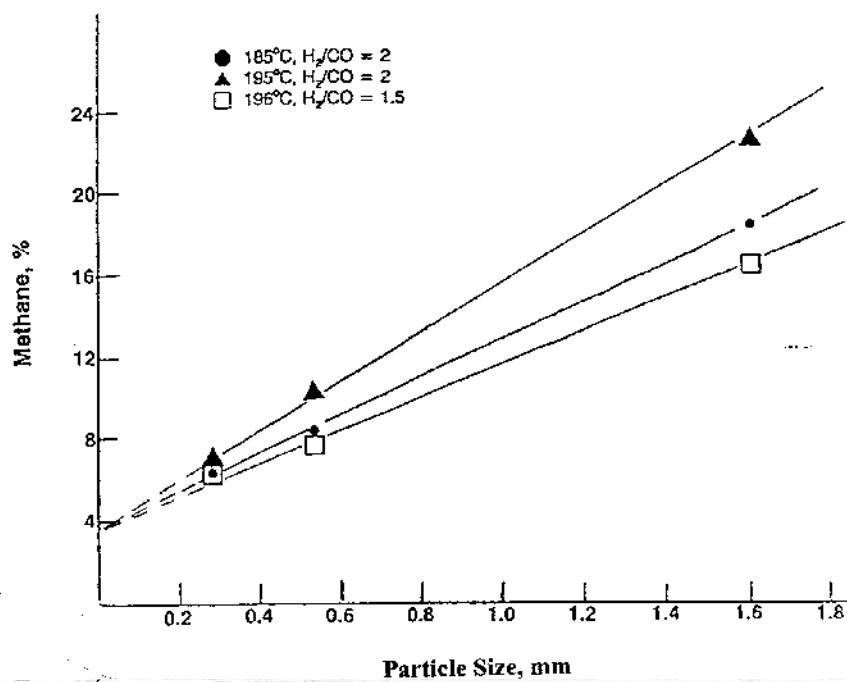
Figure XII.16.   Methane production for synthesis in fixed-bed reactor with different particle size catalysts (from XII.17).
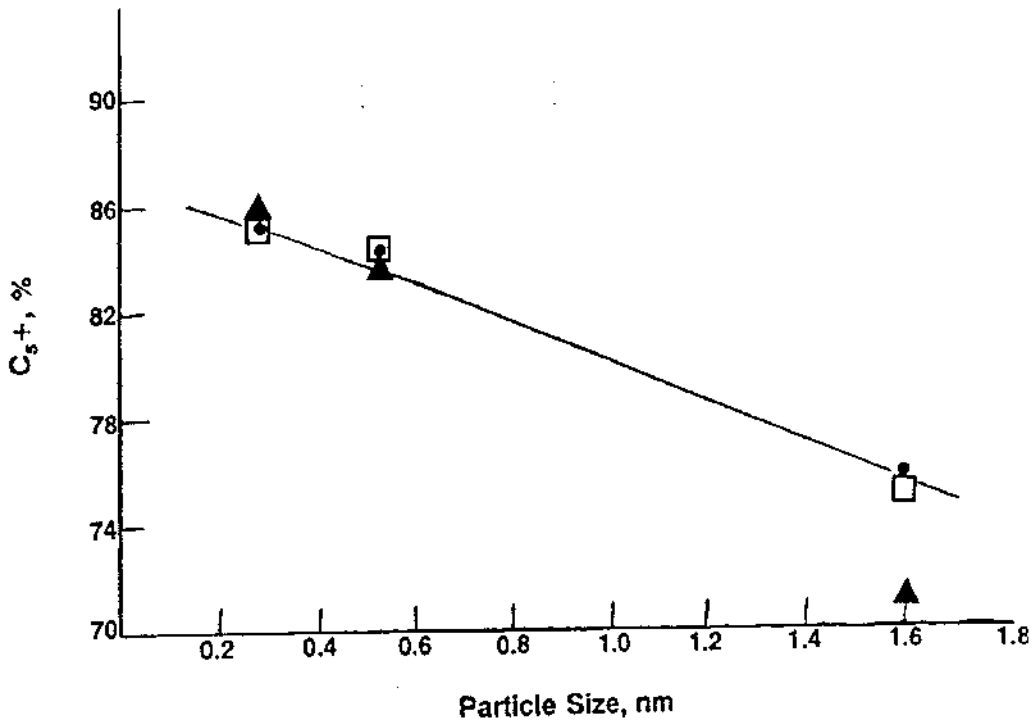
Figure XII.17. C_5+ product selectivity for three particle size catalysts in fixed-bed reactor (▲ , 185°C, H_2/CO = 2; • , 195°C, H_2/CO = 2; G, 195°C, H_2/CO = 1.5) (from XII.17).
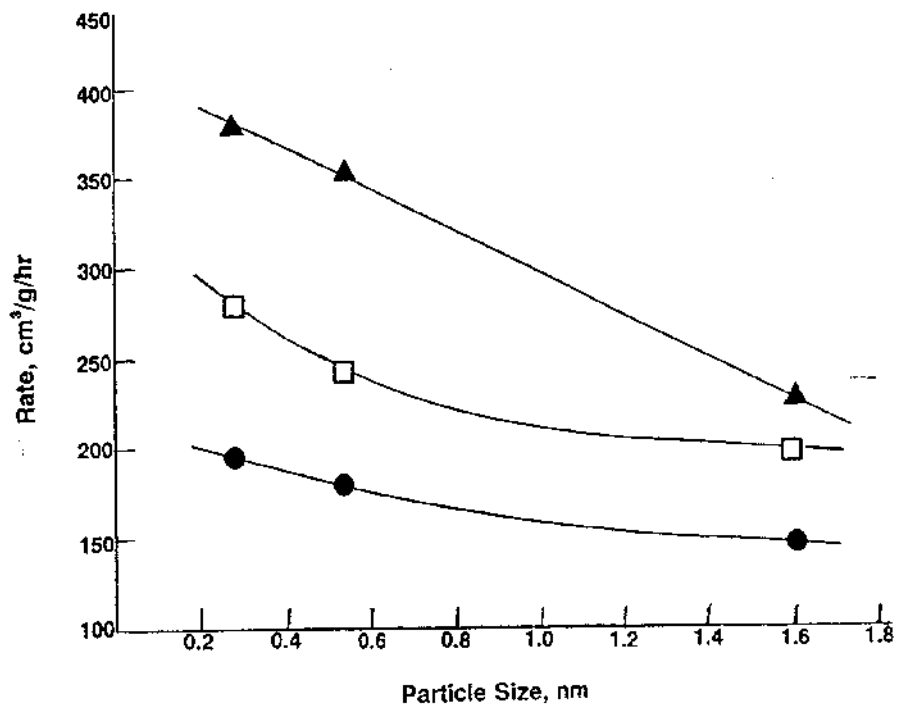
Figure XII.18.   Reaction rate for CO conversion in fixed-bed reactor for three particle size catalysts (▲ , 185°C, H_2/CO = 2; • , 195°C, H_2/CO = 2; G, 195°C, H_2/CO = 1.5) (from XII.17).
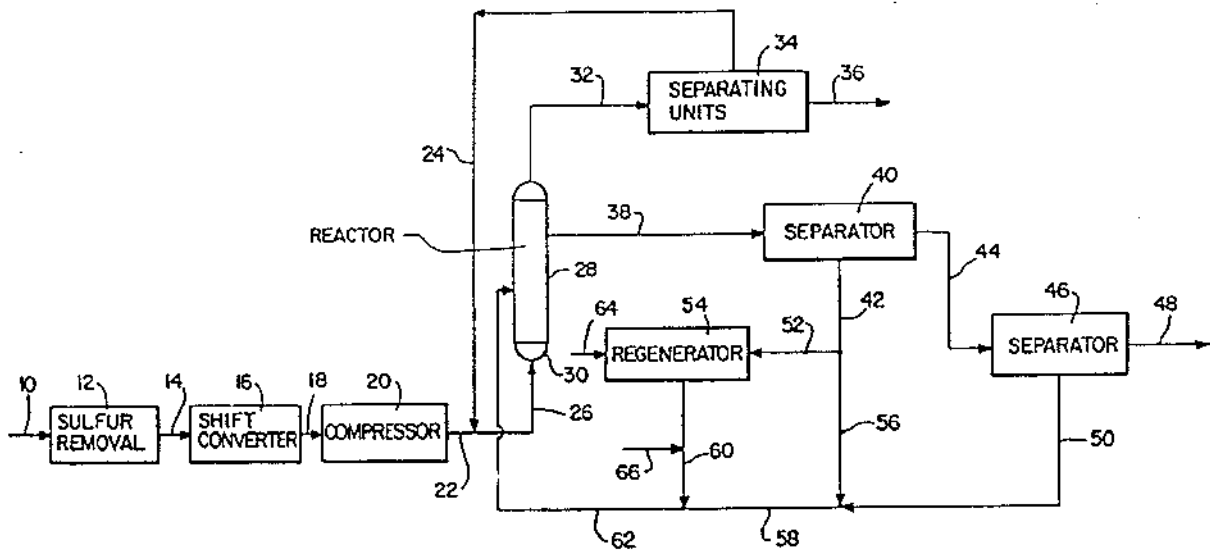
Figure XII.19.   Process schematic for slurry reactor system using cobalt catalyst
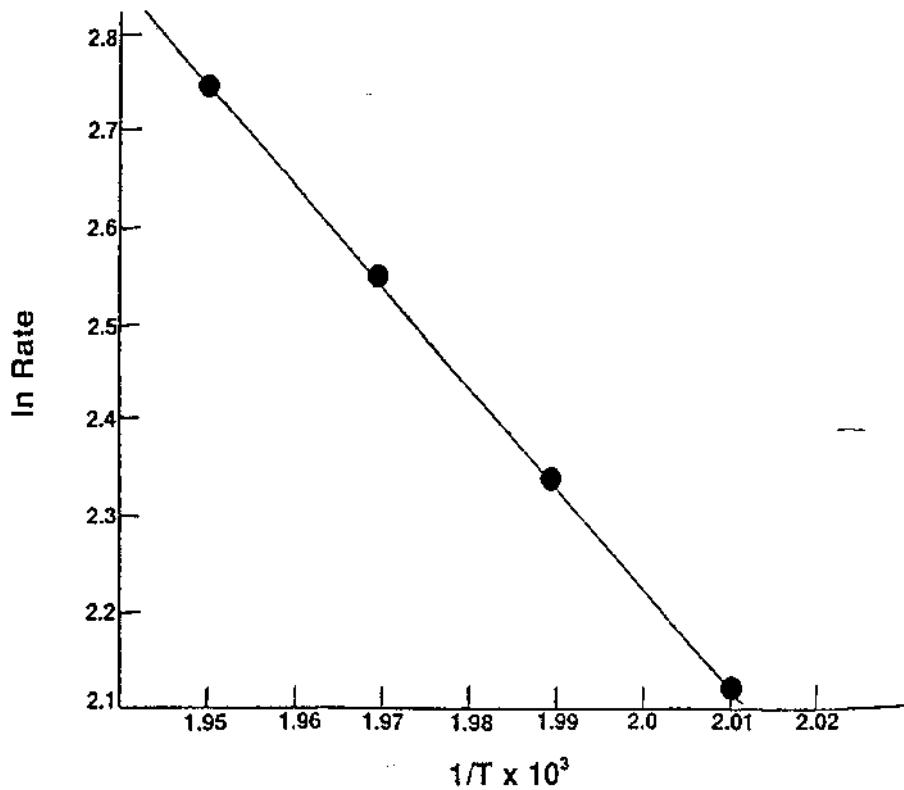(from XII.17).

Figure XII.20.   Arrhenius plot for CO conversion in slurry reactor with Co catalyst
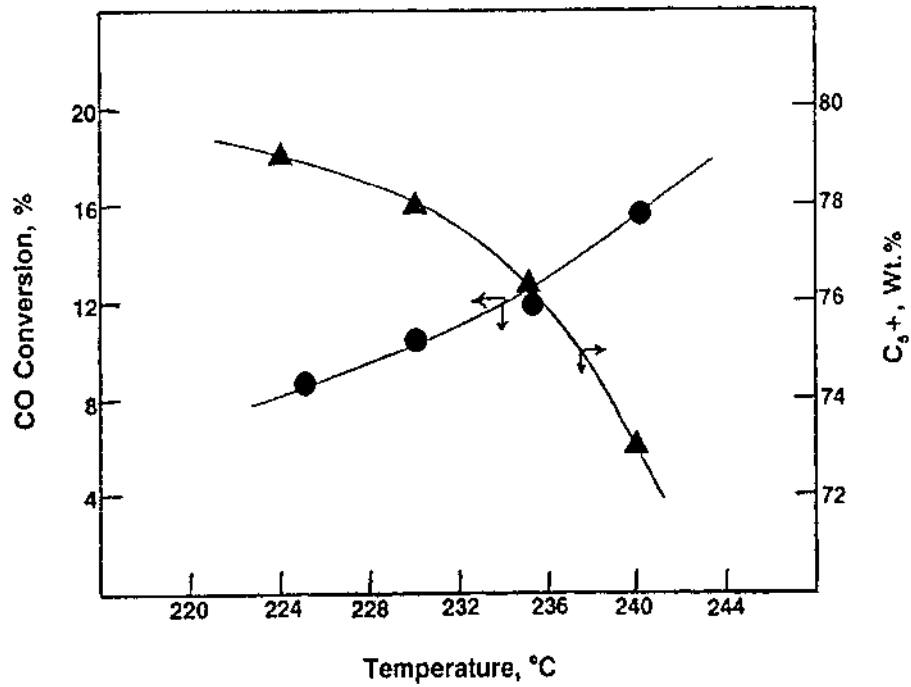(data from XII.17).

Figure XII.21. CO conversion and C_5+ product selectivity for FTS using slurry reactor and cobalt catalyst (data from XII.17).