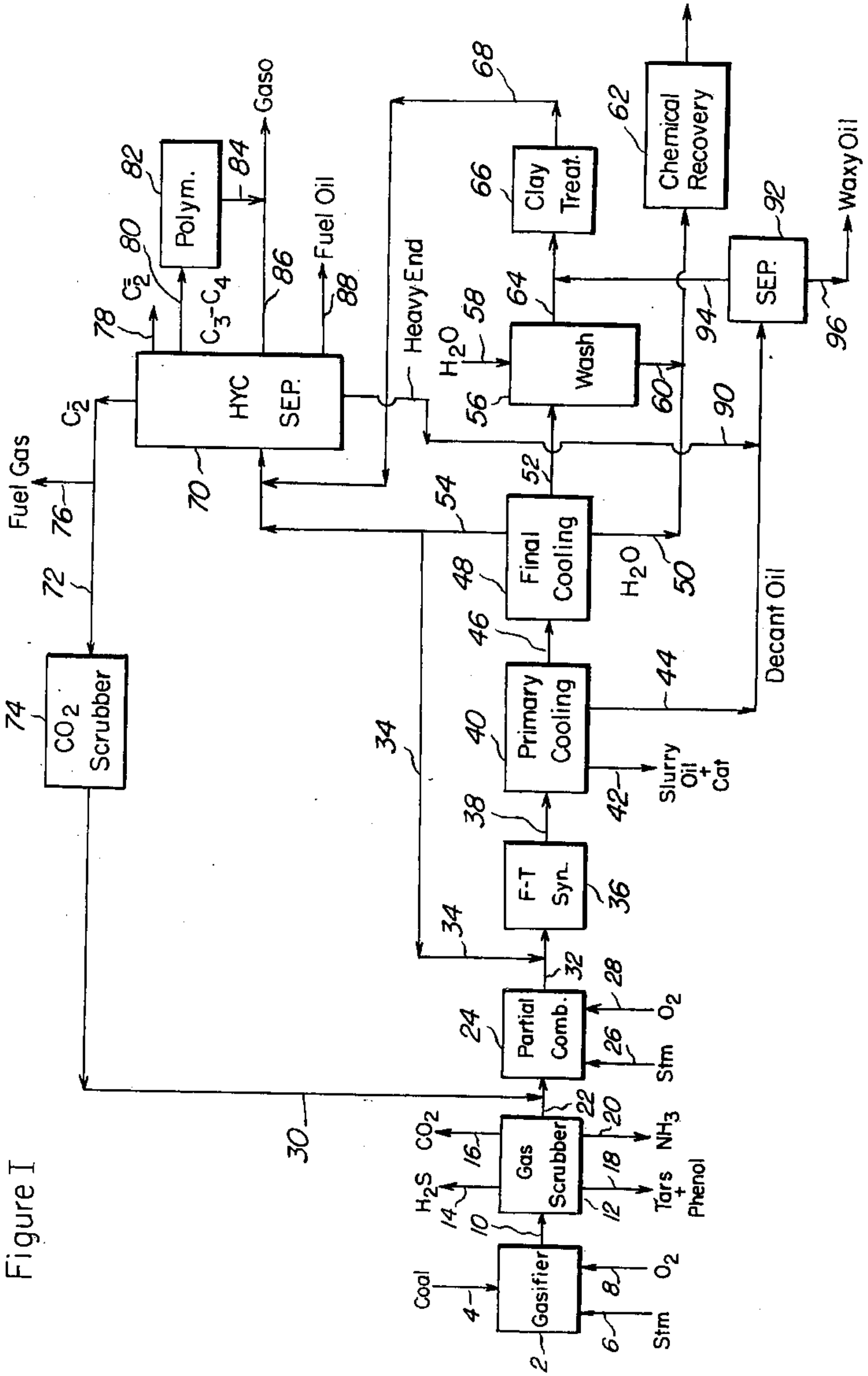

Gasifier
Coal
Stm
O_2
2
4
6
8
10
Gas Scrubber
H_2S
CO_2
14
16
12
18
20
Tars + Phenol
NH_3
22
Partial Comb.
24
26
28
Stm
O_2
30
32
34
34
F-T Syn.
36
38
Primary Cooling
40
42
Slurry Oil + Cat
44
Decant Oil
46
Final Cooling
48
H_2O
50
52
54
Wash
56
H_2O
58
60
64
Clay Treat.
66
68
Chemical Recovery
62
SEP.
92
Waxy Oil
94
96
90
HYC SEP.
70
Heavy End
78
$C_2^=$
80
C_3-C_4
Polym.
82
84
Gaso
86
Fuel Oil
88
$C_2^=$
Fuel Gas
76
72
CO_2 Scrubber
74

Figure I

Figure II

Yields Vs. Gravity of Total Liquid Product

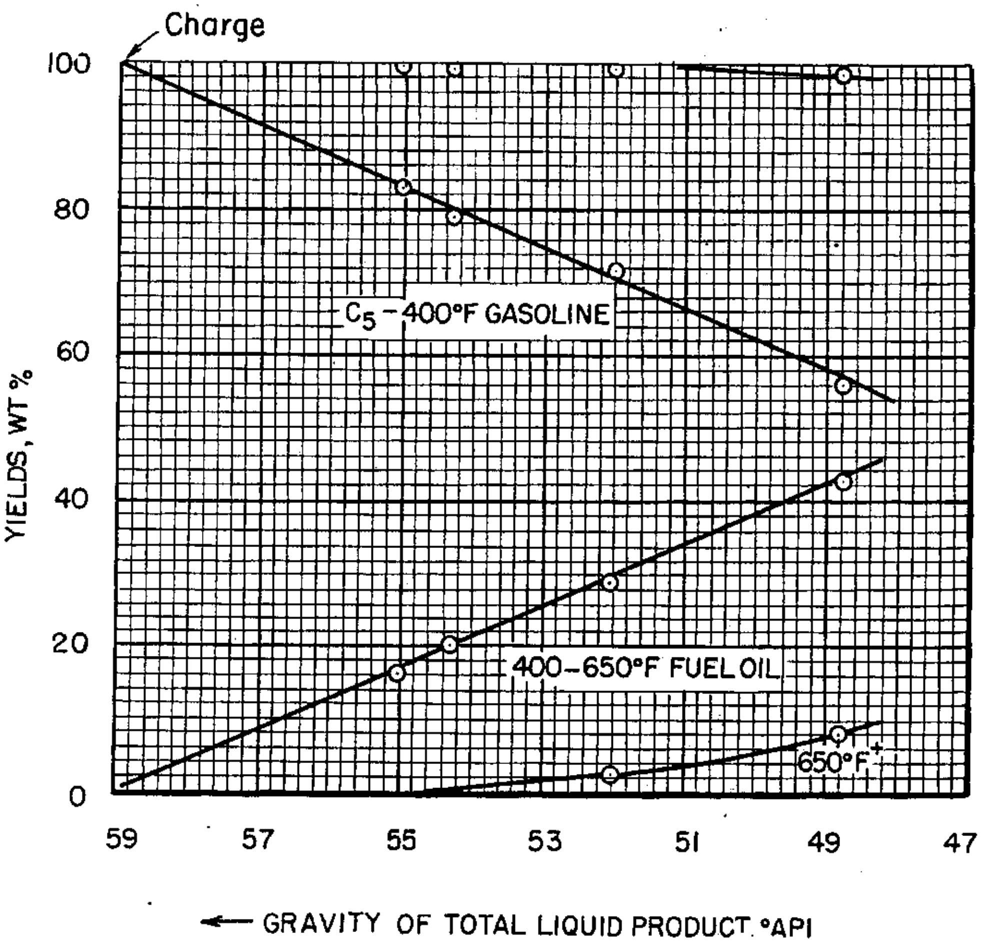
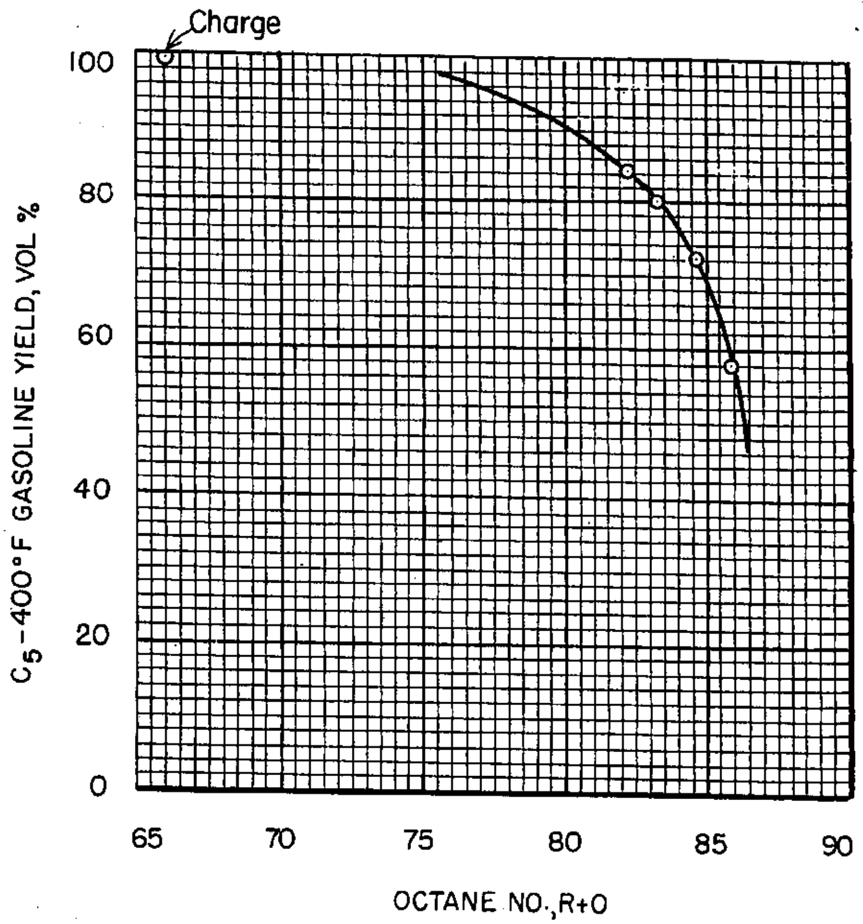


Figure III

C_5-400°F Gasoline
Yield-Octane Curve



METHOD OF UPGRADING A FISCHER-TROPSCH LIGHT OIL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is concerned with a process for converting synthesis gas, i.e. mixtures of gaseous carbon oxides with hydrogen or hydrogen donors, to hydrocarbon mixtures and oxygenates. More particularly, this invention is concerned with upgrading a C_5+ fraction having an end point of 340° up to 400° F. obtained in a known Fischer-Tropsch synthesis process, so as to obtain a high yield of C_5+ gasoline of enhanced octane and a low-pour, high diesel index fuel oil.

2. Other Prior Art

Processes for the conversion of coal and other hydrocarbons, such as natural gas to a gaseous mixture consisting essentially of hydrogen and carbon monoxide, or of hydrogen and carbon dioxide, or of hydrogen and carbon monoxide and carbon dioxide, are well known. Although various processes may be employed for the gasification, those of major importance depend either on the partial combustion of the fuel with an oxygen-containing gas or on a combination of these two reactions. An excellent summary of the art of gas manufacture, including synthesis gas, from solid and liquid fuels, is given in "Encyclopedia of Chemical Technology", edited by Kirk-Othmer, Second Edition, Volume 10, pages 353–433 (1966), Interscience Publishers, New York; the contents of which are herein incorporated by reference. The techniques for gasification of coal or other solid, liquid or gaseous fuel are not considered to be per se inventive here.

It is considered desirable to effectively and more efficiently convert synthesis gas, and thereby coal and natural gas, to highly valued hydrocarbons such as motor gasoline with high octane number, petrochemical feedstocks, liquefiable petroleum fuel gas, and aromatic hydrocarbons. It is well known that synthesis gas will undergo conversion to form reduction products of carbon monoxides, such as hydrocarbons at from about 300° F. to about 850° F. under from about one to one thousand atmospheres pressure, over a fairly wide variety of catalysts. The Fischer-Tropsch process, for example, which has been most extensively studied, produces a range of products including liquid hydrocarbons, a portion of which have been used as low octane gasoline. The types of catalysts that have been studied for this and related processes include those based on metals or oxides of iron, cobalt, nickel, ruthenium, thorium, rhodium and osmium.

The wide range of catalysts and catalysts modifications disclosed in the art and an equally wide range of conversion conditions for the reduction of carbon monoxide by hydrogen provide considerable flexibility toward obtaining selected boiling-range products. Nonetheless, in spite of this flexibility it has not proved possible to make such selections so as to produce liquid hydrocarbons in the gasoline boiling range which contain highly branched paraffins and substantial quantities of aromatic hydrocarbons, both of which are required for high quality gasoline, or to selectively produce aromatic hydrocarbons particularly rich in the benzene to xylene range. A review of the status of this art is given in "Carbon Monoxide-Hydrogen Reactions", *Encyclopedia of Chemical Technology,* edited by Kirk-Othmer, Second Edition, Volume 4, pp. 446–488, Interscience Publishers, New York, the text of which is incorporated herein by reference.

Recently, a method for upgrading the C_5+ liquid product of a Fischer-Tropsch synthesis having an end point from about 340°–400° F. has been discovered, which method comprises pretreating the C_5+ liquid product by hydrogenating it in the presence of a hydrogenation component (such as platinum or palladium) at conditions of temperature and pressure so as to selectively hydrogenate the diolefins contained in the C_5+ liquid product and thereafter contacting the hydrogenated product, at a temperature within the range of about 575° to 850° F. and at a pressure within the range of about atmospheric to 700 psig, with a crystalline aluminosilicate having certain well-defined characteristics. This method is described in a copending United States patent application, Ser. No. 684,511, filed May 7, 1976, now U.S. Pat. No. 4,052,477. It should be noted that the elevated temperatures of the step following pretreatment are such that most or substantially all of the hydrogenated product from the pretreatment step will be in the gaseous phase during the second, aluminosilicate contacting step.

SUMMARY OF THE INVENTION

This invention is concerned with improving the product distribution and yield of products obtained by a Fischer-Tropsch synthesis gas conversion process. In a particular aspect, the present invention is concerned with upgrading the C_5-400° F. liquid fraction of a synthesis gas conversion operation known in the industry as the Sasol Synthol process.

The Sasol process, located in South Africa, and built to convert an abundant supply of poor quality coal and products thereof to particularly hydrocarbons, oxygenates and chemical forming components was a pioneering venture. The process complex developed is enormous, expensive to operate and may be conveniently divided or separated into (1) a synthesis gas preparation complex from coal, (2) a Fischer-Tropsch type of synthesis gas conversion in both a fixed catalyst bed operation and a fluid catalyst bed operation, (3) a product recovery operation and (4) auxillary plant and utility operations required in such a complex.

The extremely diverse nature of the products obtained in the combination operation of the Sasol process amplifies the complexity of the overall process complex, its product recovery arrangement and its operating economics. The Sasol synthesis operation is known to produce a wide spectrum of products including fuel gas, light olefins, LPG, gasoline, light and heavy fuel oils, waxy oils and oxygenates identified as alcohols, acetone, ketones and acids, particularly acetic and propionic acid. The C_2 and lower boiling components may be reformed to carbon monoxide and hydrogen or the C_2 formed hydrocarbons and methane may be combined and blended for use in a fuel gas pipeline system.

In the Sasol operation, the water-soluble chemicals are recovered as by steam stripping distillation and separated into individual components with the formed organic acids remaining in the water phase separately treated. Propylene and butylene formed in the process are converted to gasoline boiling components as by polymerization in the presence of a phosphoric acid catalyst and by alkylation. Propane and butane on the other hand are used for LPG.

The present invention is concerned with improving a Fischer-Tropsch synthesis gas conversion operation and is particularly directed to improving the synthetic gasoline product selectively and quality obtained by processing C_5-400° F. material over a special class of crystalline zeolite represented by HZSM-5 crystalline zeolite and related catalysts. It has been found that improved benefits can be obtained with regard to such processing if the pressures and temperatures of the contacting zone are such that most of the charge and product components are in the liquid phase, thereby washing off coke precursors and minimizing the rate of catalyst aging. A particular and unexpected benefit of the "dense phase" processing as compared to the "gaseous phase" processes is that it yields a by-product, high quality fuel oil, and at the same time upgrades the C_5-400° F. material to a higher octane number. Moreover, the gas make of the method of the present invention is less than 1 percent, as compared to the 10–15 percent gas formation encountered in the "gaseous phase" processes.

Although combined oxygen in the charge is only partially removed by the present invention, complete oxygen removal is possible by a subsequent hydrotreatment of the gasoline product over a Co/Mo/Al catalyst at 50–300 p.s.i.g., 500°–600° F., 0.2–10 LHSV, and 200–700 SCF H_2/bbl, with little or no octane loss. Finally, it is not necessary to pretreat the C_5-400° F. charge by hydrogenating the diolefins contained therein.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a condensed, schematic, block-flow arrangement of a known Fischer-Tropsch syngas conversion process directed to the conversion of coal to synthesis gas comprising carbon monoxide and hydrogen and the reduction of carbon monoxide by the Fischer-Tropsch process to form a product mixture comprising hydrocarbon and oxygenates and the recovery of these products for further use.

FIG. 2 is a plot of yields of C_5-400° F. gasoline, 400°–650° F. fuel oil, and 650° F.+ product versus liquid product gravity, which plot is derived from an example of a process incorporating the present invention.

FIG. 3 is a yield-octane plot for C_5-400° F. gasoline produced in an example of a process incorporating the present invention.

DESCRIPTION OF THE INVENTION

Referring now to FIG. 1, there is shown in block flow arrangement a substantially reduced process flow arrangement of the Sasol syngas conversion process. A coal gasifier section 2 is provided to which pulverized coal is introduced by conduit 4, steam by conduit 6 and oxygen by conduit 8. The products of gasifier section 2 are then passed by conduit 10 to a gas scrubber section 12. In scrubber section 12, carbon monoxide and hydrogen-producing gases are separated from hydrogen sulfide which is removed by conduit 14, carbon dioxide removed by conduit 16, tars and phenols removed by conduit 18 and ammonia removed by conduit 20. The carbon monoxide-hydrogen producing gas is passed from section 12 by conduit 22 to a partial combustion zone 24 supplied with steam by conduit 26 and oxygen by conduit 28. Recycle C_2 fuel gas product of the combination process after separation of carbon dioxide therefrom is recycled by conduit 30 to the partial combustion section 24. In the partial combustion operation 24, a suitable carbon monoxide-hydrogen rich synthesis gas of desired ratio is formed for use in a downstream Fischer-Tropsch synthesis gas conversion operation.

The Sasol process operates two versions of the Fischer-Tropsch process; one being a fixed catalyst bed operation and the other being a fluid catalyst bed operation. Each of these operations use iron catalyst prepared and presented to obtain desired catalyst composition and activity. The synthesis gas prepared as above briefly identified is passed by conduit 32 to the Fischer-Tropsch reaction section 36 in admixture with recycle gas introduced at a temperature of about 160° C. and at an elevated pressure of about 365 psig. The temperature of the synthesis gas admixed with catalyst in the fluid operation rapidly rises by the heat liberated so that the Fischer-Tropsch and water gas shift reactions take place. The products of the Fischer-Tropsch synthesis reaction are conveyed by conduit 38 to a primary cooling section 40 wherein the temperature of the mixture is reduced to within the range of 280° to about 400° F. In a primary cooling section, a separation is made which permits the recovery of a slurry oil and catalyst stream by conduit 42, and a decant oil stream by conduit 44. In one typical operation, the decant oil stream will have an ASTM 95% boiling point of about 900° F. A light oil stream boiling below about 560° F. and lower boiling components including oxygenates is passed by conduit 46 to a second or final cooling and separating section 48. In cooling section 48, a separation is made to recover a water phase comprising water-soluble oxygenates and chemicals withdrawn by conduit 50, a relatively light hydrocarbon phase boiling below about 560° F. withdrawn by conduit 52 and a normally vaporous phase withdrawn by conduit 54. A portion of the vaporous phase comprising unreacted carbon monoxide and hydrogen is recycled by conduit 34 to conduit 32 charging syngas to the Fischer-Tropsch synthesis operation. In a typical operation, about one volume of fresh feed is used with two volumes of recycle gas. The hydrocarbons do not completely condense and an absorber system is used for their recovery. Methane and C_2 hydrocarbons are blended with other components in a pipeline system or they are passed to a gas reforming section for recycle as feed gas in the synthesis operation. The light hydrocarbon phase in conduit 52 is then passed through a water wash section 56 provided with wash water by conduit 58. In wash section 56, water-soluble materials comprising oxygenates are removed and withdrawn therefrom by conduit 60. The water phases in conduits 50 and 60 are combined and passed to a complicated and expensive-to-run chemicals recovery operation 62. The washed light hydrocarbon phase is removed by conduit 64 and passed to a clay treater 66 along with hydrocarbon fraction boiling below about 650° F. recovered from the decanted oil phase in conduit 44 and a heavy oil product fraction recovered as hereinafter described. The hydrocarbon phase thus recovered and passed to this clay treating section is preheated to an elevated temperature of above about 600° F. or higher before contacting the catalyst or clay in the treater. This clay treatment isomerizes hydrocarbons and particularly the alpha olefins in the product, thereby imparting a higher octane rating to these materials. The treatment also operates to convert harmful acids and other oxygenates retained in the hydrocarbon phase after the water wash. The clay treated hydrocarbon product is passed by conduit 68 to a hydrocarbon separation reaction 70. A portion of the hydrocarbon vapors in conduit 54 not directly recycled to the Fischer-Tropsch conversion operation by conduit **34** is also passed to the hydrocarbon separation reaction **70**. In the hydrocarbon separation section **70**, a separation is made to recover a fuel gas stream comprising C_2 hydrocarbons withdrawn by conduit **72**. A portion of this material is passed through a CO_2 scrubber **74** before recycle by conduit 30 to the partial combustion zone **24**. A portion of the fuel gas may be withdrawn by conduit **76**. In separation section **70**, a C_2 olefin rich stream is recovered by conduit **78** for chemical processing as desired. A C_3 to C_4 hydrocarbon stream rich in olefins is withdrawn by conduit **80** and passed to catalytic polymerization in section **82**. Polymerized material suitable for blending with gasoline product is withdrawn by conduit **84**. A C_5+ gasoline product fraction having an end point in the range of 340° to 360° up to 400° F. is recovered by conduit **86** and a light fuel oil product such as No. 2 fuel oil is withdrawn by conduit **90** for admixture with the decant oil fraction in conduit **44** as mentioned above. The blend of hydrocarbons product thus formed will boil in the range of about 400° F. to about 1000° F. This material blend is passed to a separator section **92** wherein a separation is made to recover a fraction boiling in the range of from about 400° to 650° F. withdrawn by conduit **44** from a heavier higher boiling waxy oil withdrawn by conduit **96**.

In this relatively complicated synthesis gas conversion operation and product recovery, it is not unusual to recover a product distribution comprising 2% ethylene, 8% LPG, 70% gasoline boiling material, 3% fuel oil, 3% waxy oil and about 14% of materials defined as oxygenates.

This Fischer-Tropsch synthesis operation above briefly defined and known in the industry as the Sasol Synthol process can be significantly improved following the concepts of this invention. It is the purpose of the invention to substantially upgrade the C_5-340° to 400° F. gasoline fraction (i.e. the product from conduit **86** prior to blending via conduit **84**) by "dense phase" processing over a special type of crystalline aluminosilicate zeolite catalyst.

The special zeolite catalysts referred to herein utilize members of a special class of zeolite exhibiting some unusual properties. These zeolites induce profound transformations of aliphatic hydrocarbons to aromatic hydrocarbons in commercially desirable yields and are generally highly effective in alkylation, isomerization, disproportionation and other reactions involving aromatic hydrocarbons. Although they have unusually low alumina contents, i.e. high silica to alumina ratios, they are very active even with silica to alumina ratios exceeding 30. This activity is surprising since catalytic activity of zeolites is generally attributed to framework aluminum atoms and cations associated with these aluminum atoms. These zeolites retain their crystallinity for long periods in spite of the presence of steam even at high temperatures which induce irreversible collapse of the crystal framework of other zeolites, e.g. of the X and A type. Furthermore, carbonaceous deposits, when formed, may be removed by burning at higher than usual temperatures to restore activity. In many environments, the zeolites of this class exhibit very low coke forming capability conducive to very long times on stream between burning regenerations.

An important characteristic of the crystal structure of this class of zeolites is that it provides constrained access to and egress from the intra-crystalline free space by virtue of having a pore dimension greater than about 5 Angstroms and pore windows of about a size such as would be provided by 10-membered rings of oxygen atoms. It is to be understood, of course, that these rings are those formed by the regular disposition of the tetrahedra making up the anionic framework of the crystalline aluminosilicate, the oxygen atoms themselves being bonded to the silicon or aluminum atoms at the centers of the tetrahedra. Briefly, the preferred zeolites useful as catalysts in this invention possess, in combination: a silica to alumina ratio of at least about 12; and a structure providing constrained access to the crystalline free space.

The silica to alumina ratio referred to may be determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with a silica to alumina ratio of at least 12 are useful, it is preferred to use zeolites having higher ratios of at least about 30. Such zeolites, after activation, acquire an intra-crystalline sorption capacity for normal hexane which is greater than that for water, i.e. they exhibit "hydrophobic" properties. It is believed that this hydrophobic character is advantageous in the present invention.

The zeolites useful as catalysts in this invention freely sorb normal hexane and have a pore dimension greater than about 5 Angstroms. In addition, their structure must provide constrained access to some larger molecules. It is sometimes possible to judge from a known crystal structure whether such constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of oxygen atoms, then access by molecules of larger cross-section than normal hexane is substantially excluded and the zeolite is not of the desired type. Zeolites with windows of 10-membered rings are preferred, although excessive puckering or pore blockage may render these zeolites substantially ineffective. Zeolites with windows of 12-membered rings do not generally appear to offer sufficient constraint to produce the advantageous conversions desired in the instant invention, although structures can be conceived, due to pore blockage or other cause, that may be operative.

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access, a simple determination of the "constraint index" may be made by continuously passing a mixture of equal weight of normal hexane and 3-methylpentane over a small sample, approximately 1 gram or less, of zeolite at atmospheric pressure according to the following procedure. A sample of the zeolite, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to testing, the zeolite is treated with a stream of air at 1000° F. for at least 15 minutes. The zeolite is then flushed with helium and the temperature adjusted between 550° F. and 950° F. to give an overall conversion between 10% and 60%. The mixture of hydrocarbons is passed at 1 liquid hourly space velocity (i.e. 1 volume of liquid hydrocarbon per volume of catalyst per hour) over the zeolite with a helium dilution to give a helium to total hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

The constraint index is calculated as follows:

$$\text{Constraint Index} = \frac{\log_{10}(\text{fraction of n-hexane remaining})}{\log_{10}(\text{fraction of 3-methylpentane remaining})}$$

The constraint index approximates the ratio of the cracking rate constants for the two hydrocarbons. Catalysts suitable for the present invention are those which employ a zeolite having a constraint index from 1.0 to 12.0. Constraint Index (CI) values for some typical zeolites, including some not within the scope of this invention are:

CAS	C.I.
ZSM-5	8.3
ZSM-11	8.7
ZSM-35	4.5
TMA Offretite	3.7
ZSM-12	2
ZSM-38	2
Beta	0.6
ZSM-4	0.5
Acid Mordenite	0.5
REY	0.4
Amorphous Silica-alumina	0.6
Erionite	38

The above-described Constraint Index is an important and even critical definition of those zeolites which are useful to catalyze the instant process. The very nature of this parameter and the recited technique by which it is determined, however, admit of the possibility that a given zeolite can be tested under somewhat different conditions and thereby have different constraint indexes. Constraint Index seems to vary somewhat with severity of operation (conversion). Therefore, it will be appreciated that it may be possible to so select test conditions to establish multiple constraint indexes for a particular given zeolite which may be both inside and outside the above-defined range of 1 to 12.

Thus, it should be understood that the "Constraint Index" value as used herein is an inclusive rather than an exclusive value. That is, a zeolite when tested by any combination of conditions within the testing definition set forth hereinabove to have a constraint index of 1 to 12 is intended to be included in the instant catalyst definition regardless that the same identical zeolite tested under other defined conditions may give a constraint index value outside of 1 to 12.

The class of zeolites defined herein is exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-21, ZSM-35, ZSM-38 and other similar material. Recently issued U.S. Pat. No. 3,702,886 describing and claiming ZSM-5 is incorporated herein by reference.

ZSM-11 is more particularly described in U.S. Pat. No. 3,709,979, the entire contents of which are incorporated herein by reference.

ZSM-12 is more particularly described in U.S. Pat. No. 832,449, the entire contents of which are incorporated herein by reference.

U.S. application Ser. No. 358,192, filed May 7, 1973, now U.S. Pat. No. 4,016,245 the entire content of which are incorporated herein by reference, describes a zeolite composition and a method of making such, designated as ZSM-21 which is useful in this invention.

U.S. application Ser. No. 528,061, filed Nov. 29, 1974, the entire contents of which are incorporated herein by reference, describes a zeolite composition including a method of making it. This composition is designated ZSM-35 and is useful in this invention.

U.S. application Ser. No. 528,060, filed Nov. 29, 1974 and now abandoned, the entire contents of which are incorporated herein by reference, describes a zeolite composition including a method of making it. This composition is designated ZSM-38 and is useful in this invention.

The X-ray diffraction pattern of ZSM-21 appears to be generic to that of ZSM-35 and ZSM-38. Either or all of these zeolites is considered to be within the scope of this invention.

The specific zeolites described, when prepared in the presence of organic cations, are substantially catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 1000° F. for one hour, for example, followed by base exchange with ammonium salts followed by calcination at 1000° F. in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of this special type zeolite; however, the presence of these cations does appear to favor the formation of this special type of zeolite. More generally, it is desirable to activate this type zeolite by base exchange with ammonium salts followed by calcination in air at about 1000° F. for from about 15 minutes to about 24 hours.

Natural zeolites may sometimes by converted to this type zeolite by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, alone or in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite, dachiardite, epistilbite, heulandite and clinoptilolite. The preferred crystalline aluminosilicates are ZSM-5, ZSM-11, ZSM-12 and ZSM-21, with ZSM-5 particularly preferred.

The zeolites used as catalysts in this invention should be essentially in the hydrogen form. They may be base exchanged or impregnated to contain a Group VIII metal for enhanced stability. It is desirable to calcine the zeolite after base exchange. The metal cations that may be present include any of the cations of the metals of Group VIII of the periodic table.

In a preferred aspect of this invention, the zeolites useful as catalysts herein are selected as those having a crystal framework density, in the dry hydrogen form, of not substantially below about 1.6 grams per cubic centimeter. It has been found that zeolites which satisfy all three of these criteria are most desired. Therefore, the preferred catalysts of this invention are those comprising zeolites having a constraint index as defined above of about 1 to 12, a silica to alumina ratio of at least about 12 and a dried crystal density of not substantially less than about 1.6 grams per cubic centimeter. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstroms, as given, e.g. on page 19 of the article on Zeolite Structure by W. M. Meier. This paper, the entire contents of which are incorporated herein by reference, is included in "Proceedings of the Conference on Molecular Sieves, London, April 1967" published by the Society of Chemical Industry, London, 1968. When the crystal structure is unknown, the crystal framework density may be determined by classical pyknometer techniques. For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. It is possible that the unusual sustained activity and stability of this class of zeolites is associated with its high crystal anionic framework density of not less than about 1.6 grams per cubic centimeter. This high density, of course, must be associated with a relatively small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, seems to be important as the locus of catalytic activity.

Crystal framework densities of some typical zeolites including some which are not within the purview of this invention are:

Zeolite	Void Volume		Framework Density	
Ferrierite	0.28	cc/cc	1.76	g/cc
Mordenite	.28		1.7	
ZSM-5, -11	.29		1.79	
Dachiardite	.32		1.72	
L	.32		1.61	
Clinoptilolite	.34		1.7	
Laumontite	.34		1.77	
ZSM-4 (Omega)	.38		1.65	
Heulandite	.39		1.69	
P	.41		1.57	
Offretite	.40		1.55	
Levynite	.40		1.54	
Erionite	.35		1.51	
Gmelinite	.44		1.46	
Chabazite	.47		1.45	
A	.5		1.3	
Y	.48		1.27	

As has heretofore been stated, the most preferred form of the specific, previously defined zeolites in carrying out the novel process of this invention is the hydrogen form. As acid form is well known in the art, the hydrogen form can be made by base exchanging the particular zeolite with hydrogen ions or ions capable of conversion to hydrogen ions, i.e. ammonium ions.

The crystalline zeolite compositions can also be admixed with a non-acidic inorganic binder, such as alumina in order to impart the desired properties to the zeolite, such as increased strength and attrition resistance. Quite obviously, the proportion of binder employed is not narrowly critical, and it has been found convenient to use compositions where the binder is present from about 10 to 70% and preferably 30–40% based on the total weight of the zeolite plus binder.

By the term "dense phase" processing, as used herein, is meant the maintenance of most of the charge and product in contact with the catalyst of this invention is the liquid phase. The quantity of charge and product present in the liquid phase is preferably greater than 90 percent of the total quantity of charge and product in contact with the catalyst. The operating conditions of the dense phase technique are pressures of 200 to 1000 psig, no hydrogen, temperatures of the order of 400° to 700° F. and LHSV of 0.1 to 2. As was mentioned previously, the primary purpose of the technique is to minimize catalyst aging by allowing the liquid phase charge and product to "wash off" coke precursors from the catalyst surface. Preferred operating conditions are

pressures of 600 to 700 psig, no hydrogen, temperatures of 450° to 560° F. and LHSV of 0.1 to 1.0.

Since a pure gas at temperature above its critical temperature cannot be liquefied, regardless the degree of compression, it is essential that the temperature of process of this invention be well below the critical point of the mix present in the catalyst contacting zone. The critical point of the mix represents the condition at which the specific properties of the liquid and gas phases become identical, causing the phases to be indistinguishable. To indicate the range of the critical properties of the substances contained in C_5-400° F. charge and the products of the process of this invention, the following properties of various hydrocarbons have been selected from F. P. Rossini et al., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburgh, Pennsylvania, 1953:

Pentene-1	394° F	586 psi
n-Pentane	386° F	490 psi
n-Hexane	455° F	440 psi
n-Heptane	512° F	397 psi
n-Octane	565° F	362 psi
n-Nonane	611° F	331 psi
n-Decane	654° FG	306 psi

Critical properties for olefins greater than C_5 were not included by Rossini but may be estimated by methods such as the one described by Gambill in *Chemical Engineering*, June 15, 1959, pp. 182–83; and *Chemical Engineering*, July 13, 1959, pp. 157–160; or by Nokay in *Chemical Engineering, Feb.* 23, 1959, p. 146.

The following example illustrates the best mode now contemplated for carrying out this invention.

EXAMPLE I

A C_5-400° F. liquid fraction product of Fischer-Tropsch synthesis was passed over HZSM-5 extrudate at 700 psig, 0.6–1 LHSV, and temperatures of 450°–560° F. for a period of 21 days. Properties of the C_5-400° F. charge are shown in Table I. The HZSM-5 extrudate contained 35 percent alumina binder, was sized to 30–60 mesh, and was charged to a 9/32 inches i.d. S.S. tubing reactor where it was pretreated with hydrogen at 900° F. for one hour. After catalyst pretreatment, the reactor was pressured to 700 psig with nitrogen against a groove loader, and then the C_5-400° F. charge pumped down-flow over the catalyst bed at reaction temperature. The run was started at 450° F., under which condition all components except the C_5's were liquid. At 560° F. the C_8+ components remain in the liquid phase, but at temperatures above 560° F. aging rates would be expected to accelerate because of the loss of the "dense phase" condition characteristic of this invention. Analysis of the C_5 components concentrated in the liquid product was accomplished by the gas chromatographic technique, and the liquid product was fractionated in Vigereaux column with cut points at 400° and 650° F. Results of the Example are summarized in Table I:

TABLE I

Time on Stream, Days	Charge	7	8	14	21
Process Conditions					
LHSV	—	0.60	0.62	0.62	0.58
Average Temp., ° F	—	506	453	506	505
Properties of Total Liquid Product					
Gravity, ° API	58.9	48.8	54.3	52.1	55.1
Oxygen, wt. %	1.6	0.7	0.7	—	—
Yields, wt. % of Oil Charge					
C_1 -C_4	0.1	1.5	0.6	0.2	0.3

TABLE I-continued

Time on Stream, Days	Charge	7	8	14	21
C_5, total	4.1	2.5	2.8	2.2	3.4
C_5, olefinic	3.5	0.9	1.0	1.4	2.8
C_6+	95.8	96.0	96.6	97.6	96.3
C_6 Olefin Distribution, wt. % of Total C_5 Olefinic Yield					
1-Pentene	75	<1	<1	2	6
2-Methyl-1-butene	9	17	17	15	7
3-Methyl-1-butene	6	<1	<1	1	1
trans-2-Pentene	4	10	10	16	42
cis-2-Pentene	4	4	5	7	19
2-Methyl-2-butene	2	69	68	59	25
Properties of Liquid Product Fractions					
C_5-400° F Gasoline					
wt.% of charge	100	55.2	79.1	71.0	82.7
Gravity, ° API	66.0	85.9	83.3	84.7	82.3
Octane No. (R+O)	66.0	85.9	83.3	84.7	82.3
Oxygen, wt. %	1.6	0.8	0.8	0.9	0.9
400–650° F Fuel Oil					
wt. % of Charge	—	35.2	20.3	26.1	17.0
Gravity, ° API	—	42.6	38.0	42.0	36.3
Pour Point, ° F	—	<−70	<−65	<−70	<−70
Aniline No. ° F	—	147.8	131.5	142.0	124.0
Diesel Index	—	63.0	50.0	59.6	45.4
650° F + Product					
wt. % of Charge	—	8.1	—	2.7	—

Gravity of the total (i.e. unfractionated) liquid product was used to monitor conversion of the C_5-400° F. liquid fraction from the Fischer-Tropsch synthesis to higher boiling products and also to monitor catalyst aging. FIG. II is a plot of yields of C_5-400° F. gasoline, 400° F.–650° F. fuel oil, and 650° F. product versus total liquid product gravity, °API.

Another indicator of catalyst activity in the process of this invention is the C_5 olefin composition. For example, an examination of the data included in Table I indicates an increase in the 1-Pentene content and a corresponding decrease in the 2-Methyl-2-butene content of the product C_5 olefins after 21 days on stream. From this information, some catalyst aging may be inferred. However, a pump failure occurred early in the run resulting in an approximately 25 hour soak at 550° F., which would be expected to deposit coke on the catalyst. Nevertheless, considering the fact that the catalyst was functioning well at 500° F. after 14 days of operation despite the experimental shortcomings, it is both reasonable and justifiable to expect that the dense phase process of this invention will effect at least a 1-month catalyst cycle at the 70%+ gasoline yield level.

The yield-octane plot for C_5-400° F. gasoline product, shown in FIG. III, shows a 12 volume percent yield loss to 400°–650° F. fuel oil product for the first 15 octane number increase (i.e. from 66 to 81 R.O.N.). Little further increase beyond 85 R.O.N. (R+O) is expected regardless of further gasoline loss and this expectation is supported by FIG. III. This relationship is predictable because of the existence of residual, low-octane paraffins, which are not reacted. Rapid isomerization of the 1-olefins, along with polymerization to the 400°–650° F. fuel oil product accounts for the rapid initial octane gain. However, further octane gain requires disappearance of the slower-polymerizing, internal and branched olefins plus further isomerization. Finally, the following mass spectrographic P/O/N/A analyses of the C_4-400° F. gasoline products (see Table II) show that aromatic content increases with octane number, but this increase can be accounted for primarily by the concentration of the original aromatics in the feed — not the formation of additional aromatic compounds.

TABLE II

P/O/N/A Analyses of Gasoline Products				
Gasoline Yield, wt. %	100	79	71	55
Days on Stream (See Table I)	Charge	8	14	7
Paraffins, Vol. %	9	10	15	18
Olefins, Vol. %	—	82	68	56
Naphthenes, Vol. %	—	1	2	3
Aromatics, Vol. %	—	7	15	23
Octane No. (R+O)	66	83.3	84.7	85.9

The properties of the 400°–650° F. fuel oil product are shown below in Table III as a function of the severity of dense phase processing.

TABLE III

400–650° F Product Yield	20	26	35
Days on Stream (see Table I)	8	14	7
Gravity, ° API	38.8	42.0	42.6
Boiling Range, ° F (Simulated Distillation, ASTM Method D-2887)			
10%	—	421	422
50%	—	510	497
90%	—	613	600
98%	—	661	637
Pour Point, ° F	<−65	<−70	<−70
Aniline No., ° F	131.5	142.0	147.8
Diesel Index	50	60	63

The data in Table III, particularly the low pour points coupled with the high aniline numbers, indicate that the 400°–650° F. product is a highly-branched, non-aromatic fuel. Furthermore, when the total 400° F.+ product after 7 days on stream was collected, it was found to have a pour point of −75° F., an aniline number of 152.5, a gravity of 40.5 °API, and a diesel index of 62. Thus, the 650° F.+ product may be included in the 400° F. product and the resulting 400° F.+ fraction used as a No. 2 fuel oil. However, the 650° F.+ product by itself is probably of limited commerical importance because of its low viscosity index (the 650° F.+ fraction after 7 days on stream had a pour point of −20° F., a kinetic viscosity at 100° F. of 26.64 cs, a kinetic viscosity at 210° F. of 4.50 cs., and a viscosity index of 82).

What is claimed is:

1. In a method for upgrading a product of Fischer-Torpsch synthesis boiling within the range of C_5 to 400° F. to gasoline and fuel oil product by contacting a crystalline aluminosilicate catalyst characterized by a pore

dimension greater than 5 Angstroms, a silica to alumina ratio of at least 12 and a constraint index within the range of 1 to 12, the improvement which comprises,

(a) effecting contact of said Fischer-Tropsch synthesis product boiling within the range of C_5 to 400° F. maintained at least 90 percent in liquid phase with said crystalline aluminosilicate catalyst in the absence of hydrogen at a pressure within the range of 200 to 1000 psig, maintaining the temperature during said contact within the range of 400° to 560° F. and a liquid hourly space velocity within the range of 0.1 to 2, and

(b) recovering a C_5 plus gasoline product of improved octane and a fuel oil product from said liquid phase upgrading operation.

2. The method of claim 1 wherein the temperature is at least 450° F. and the space velocity is below 1.0.

3. The method of claim 1 wherein the crystalline aluminosilicate is exchanged with one of hydrogen ions or ammonium ions.

4. The method of claim 1 wherein the crystalline aluminosilicate is selected from the group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-35 and ZSM-38.

5. The method of claim 1 wherein the gasoline product is hydrotreated in the presence of a cobalt-molybdenum-alumina catalyst to produce a deoxygenated gasoline product.

6. The method of claim 1 wherein the zeolite is ZSM-5 and is composited with an inorganic oxide binder.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 4,126,644 Page 1 of 2

DATED : November 21, 1978

INVENTOR(S) : Philip D. Caesar et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3,	Line 2	"selectively" should be "selectivity"
7	59	"832,449" should be "3,832,449"
7	62	Delete "now U. S. Pat. No. 4,016,245"
7	62	"content" should be "contents"
9	20	"1.7" should be "1.71"
9	48	"is" should be "in"
9	58	"to" should be "of"
10	3	"temperature" should be "temperatures"
10	25	"654° FG" should be "654° F"
10	47	"groove" should be "grove"
10	57	Insert "a" after "in"

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

Page 2 of 2

PATENT NO. : 4,126,644
DATED : November 21, 1978
INVENTOR(S) : Philip D. Caesar et al

It is certified that error appears in the above–identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 11,	Line 6	"C_6 olefin" should be "C_5 olefin"
11	18	"66.0, 85.9, 83.3, 84.7, 82.3" should be "58.9, 55.9, 58.2, 56.9, 58.6" respectively
11	63	"C_4" should be "C_5"
12	53	"-75° F." should be "<-75° F."
12	56	"400° F." should be "400-650° F."
12	66	"Torpsch" should be "Tropsch"

Signed and Sealed this

Twenty-fourth **Day of** *April 1979*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

DONALD W. BANNER
Commissioner of Patents and Trademarks