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(54) Improved Fischer-Tropsch process for providing increased diesel and heavy hydrocarbon yield

(57) In a process, operated in the fluid mode, for producing increased diesel and heavier hydrocarbon yields from synthesis gas there is used a Fischer-Tropsch synthesis catalyst and a zeolite. Preferably there is used a catalytic mixture comprising a minor amount of a zeolite catalyst which selectively converts enough waxy product to prevent adhesion between catalyst particles which might interfere with catalyst flow thereby permitting maximization of diesel oil and heavy hydrocarbon yields.

SPECIFICATION

Improved Fischer-Tropsch process for providing increased diesel and heavy hydrocarbon yield

This invention is directed to an improved Fischer-Tropsch process for hydrocarbon synthesis operated in the fluid mode of the Sasol Synthol process to provide increased diesel and heavy hydrocarbon yield. In another aspect, it is directed to the utilization of Fischer-Tropsch synthesis catalysts modified by the presence of a minor amount of a zeolite catalyst.

In the Synthol version of the Fischer-Tropsch process, the catalyst particles are moving in a fluidized or entrained bed. This has many engineering and operating advantages over the use of a fixed bed, in particular with respect to temperature control, good mixing, heat removal, prevention of large temperature gradients, ease in changing or maintaining the desired catalyst, etc.

U.S. 4,046,829 is directed to a Fischer-Tropsch synthesis comprising separating the product into a fraction boiling above and below 204°C (400°F) and separately processing each over crystalline aluminosilicate zeolite. U.S. 4,052,477 is directed to a Fischer-Tropsch synthesis wherein a C_6^+ fraction is separated, hydrogenated and contacted with a zeolite to obtain higher octane gasoline. U.S. 4,207,208 discloses single particle iron-containing syngas conversion catalysts comprising iron and a crystalline acidic aluminosilicate zeolite.

The patent and technical literature relating to the Fischer-Tropsch process is extensive and the various catalysts reported in the prior art have been used by themselves as well as in admixture with catalytically inactive supports such as kieselguhr. U.S. Patent No. 4,086,262 is primarily directed to a multi-particle composite catalyst wherein the crystalline aluminosilicate component is physically admixed with a particulate Fischer-Tropsch catalytic component and to a process of converting synthesis gas to aromatics rich hydrocarbon mixtures or to hydrocarbon mixtures rich in liquefiable petroleum gases. In spite of the flexibility of these prior art processes, it has not been possible to efficiently and at relatively low cost provide as great a quantity of high quality diesel fuels as is desired.

The present invention, therefore, is concerned with a Fischer-Tropsch process wherein diesel range hydrocarbon product yield is maximized comprising in a fluidized bed the simultaneous use of a Fischer-Tropsch synthesis catalyst and a zeolite catalyst of critical type, amount and activity such that the synthesis reactor operates at below the temperature minimum required in the prior art fluidized bed (Synthol) Fischer-Tropsch process, without loss of particle fluidization and flow characteristics. The zeolite catalyst must be of just sufficient activity and in just that relative amount to selectively convert enough waxy product to prevent adhesion between catalyst particles which otherwise might impede catalyst flow, and without causing extensive dewaxing conversion across the major portion of the boiling range of products.

More particularly, the process of the present invention is directed towards improving product yield, obtaining a larger yield of diesel fuel range materials, and improving operating economies of a synthesis gas conversion operation known in the industry as the Sasol process.

The Sasol process converts coal to hydrocarbons, oxygenates and chemical forming components. It is conveniently separated into (1) a synthesis gas preparation from coal, (2) a Fischer-Tropsch (F-T) type of synthesis gas conversion in both a fixed catalyst bed operation (ARGE Process) and a fluid catalyst bed operation (Synthol Process), (3) a product recovery operation and (4) product upgrading, refining and separation. The fixed bed process uses an expensive tube and shell heat exchange reactor and operates at temperatures between 210-230°C (410° to 446°F). It provides undesirably high amounts of paraffin waxes. The moving bed Synthol process is more economical but is limited to operating at temperatures of 310-330°C (590° to 626°F) and essentially all the product is in the gaseous state. Consequently light gases and gasoline are the major products. However, less than 10% diesel fuel is typically contained in its products. The instant process is an improvement thereof producing up to 45% or more diesel.

The Sasol synthesis operation is known to produce a wide spectrum of products which amplify the complexity of the overall process arrangement and its operating economics. Aside from the hydrocarbon liquids which include gasoline, light and heavy fuels, fuel gas, light olefins, liquefied petroleum gas (LPG) and waxy oils, these are produced and identified as alcohols, aldehydes, ketones and acids (particularly acetic and proprionic acid). The C_2 and lower boiling components may be reformed to synthesis gas or they may be blended into a fuel gas pipeline system.

Propylene and butylene formed in the process can be further converted to fuel liquids as by polymerization in the presence of a solid phosphoric acid catalyst, which process produces primarily more gasoline. Higher amounts of gasoline can be made by involving zeolite catalysts either in combination with the Fischer-Tropsch synthesis operation, or in a subsequent conversion process involving certain parts or all of the synthesis product. Many such methods have been described. Current Fischer-Tropsch technology accordingly suffers from severe constraint on the relative amount of diesel fuel product compared to the volume of gasoline that can be produced.

In no case known to the present inventors has the use of zeolite in a Fischer Tropsch synthesis operation been suggested or utilized to increase the amount of diesel fuel relative to gasoline.

The present invention is concerned with improving a moving bed Fischer-Tropsch synthesis gas conversion operation such as the Synthol process wherein the product distribution is changed in favor of the diesel distillate range by utilizing the herein described modified Fischer-Tropsch catalyst. The improved process in accordance with this invention utilizes a specific range of conversion conditions, specific zeolite particle and granule sizes, and wherein Fischer-Tropsch catalysts are modified with specific zeolite percentages and alpha values. More particularly the present invention is concerned with improving the diesel and heavier distillate fuel yield of a Fischer-Tropsch type conversion operation.

Proper operation of the charge of moving catalyst particles places a restriction on the lowest temperature at which the Fischer-Tropsch synthesis can be operated. The synthesis process produces a wide range of hydrocarbons, ranging in molecular size from gases to waxy molecules. As the temperature is lowered there is an inherent tendency in the Fischer-Tropsch process to shift the distribution of products towards higher boiling materials. This would, in principle, result in a relatively larger diesel fuel fraction, except for the fact that more waxes are also made; and the highest molecular weight wax molecules are liquid under the operating conditions and tend to condense on the surface of catalyst particles. The coating of catalyst particles with wax leads to sticking and adhesion among particles which interferes with the free flow of the catalyst particles and leads to inoperability.

This represents a serious limitation to attempts to increase the fraction of heavier than gasoline type fuels such as diesel oils, by an economically advantageous fluidized bed process. Current trends toward more diesel production in view of this is actually forcing abandonment of the otherwise desirable fluid bed principle, and partial return to consideration of the fixed bed technology.

A shape-selective zeolite catalyst component is added to a Fischer-Tropsch synthesis catalyst charge such that just sufficient amounts of heavy wax molecules are selectively cracked to prevent laydown of wax on catalyst which would interfere with fluidization whereby the system is operated at lower than usual temperature conditions, obtaining a higher diesel distillate-to-gasoline ratio. Accordingly, the method in accordance with the invention maximizes the production of diesel oil and heavier hydrocarbons comprising operating a fluid mode Fischer-Tropsch synthesis process in the presence of a catalyst system comprising a major proportion of a Fischer-Tropsch synthesis catalyst and a minor proportion of an aluminosilicate zeloite catalyst having a silica to alumina ratio of at least 12, a constraint index of from 1 to 12 wherein the fraction of zeolite catalyst used, zeolite activity and the amount of liquid product produced under specified operating conditions of time, temperature and pressure and controlled in accordance with the following equation:

$$f . \alpha . W = A . n$$

which is more fully described herein below, thereby selectively converting sufficient waxy product to prevent adhesion between catalyst particles and maintain catalyst fluidity.

It is to be understood that any suitable conventional Fischer-Tropsch catalyst may be used in this invention. Types of catalysts found useful in Fischer-Tropsch syntheses include but are not limited to, the following metals: iron, cobalt, ruthenium, thorium, osmium or rhodium, mixtures or suitable compounds thereof. Compounds especially preferred are iron oxides and iron carbides. The Fischer-Tropsch catalysts may also comprise particles of any of the recited metals only or particles with minor amounts of K, Cu, Sn, P, W, rare earth, V, Mn, Mo, etc.

The zeolitic catalysts referred to herein are members of a special class of zeolites exhibiting some unusual properties. 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 aluminium atoms and cations associated with these aluminium 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 of very long times on stream between burning regenerations.

An important characteristic of the crystal structure of this novel class of zeolites is that it provides a selective constrained access to and egress from the intracrystalline free space by virtue of having an effective pore size intermediate between the small pore Linde A and the large pore Linde X zeolites, i.e. the pore windows of the structure are of a size such as would be provided by 10-membered rings of silicon atoms interconnected by 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 zeolite, the oxygen atoms themselves being bonded to the silicon (or aluminium, etc.) atoms at the centers of the tetrahedra.

The silica to alumina mole 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 aluminium in the binder or in cationic or other form within the channels. Although zeolites with silica to alumina mole ratios of at least 12 are useful, it is preferred in some instances to use zeolites having higher ratios of at least 30. Such zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than for water, i.e., they exhibit "hydrophobic" properties. It is believed that this hydrophobic characteristic 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 5 Angstroms. In addition, the structure must provide constrained access to 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 excluded and the zeolite is not of the desired type. Zeolites with windows of 10-membered rings are preferred, although in some instances excessive puckering of the rings or pore blockage may render these zeolites ineffective. Zeolites with windows of 12-membered rings do not offer sufficient constraint to produce advantageous conversions desired in the instant invention, although structures can be conceived due to pore blockage or other causes, that may be operative.

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary constrained access to molecules of larger cross-section than normal paraffins, a simple determination of the "Constraint Index" is made.

The Constraint Index approximates the ratio of the cracking rate constants for the two hydrocarbons. Zeolites suitable for the present invention are those having a Constraint Index of 1 to 12. Constraint Index (CI) values for some typical zeolites are:

Zeolite	*C.I.*
Erionite	38
ZSM-4	0.5
ZSM-5	8.3
ZSM-11	8.7
ZSM-12	2
ZSM-35	4.5
ZSM-38	2
TMA Offretite	3.7
Beta	0.6
H-Zeolon (mordenite)	0.4
REY	0.4
Amorphous Silica-Alumina	0.6

The above-described Constraint Index is an important and even critical definition of those zeolites which are useful in the instant invention. 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 are thereby exhibit different Constraint Indices. Constraint Index seems to vary somewhat with severity of operation (conversion) and the presence or absence of binders. Likewise, other variables such as crystal size of the zeolite, the presence of occluded contaminants, etc., may affect the constraint index. Therefore, it will be appreciated that it may be possible to so select test conditions as to establish more than one value in the range of 1 to 12 for the Constraint Idex of a particular zeolite. Such a zeolite exhibits the constrained access as herein defined and is to be regarded as having a Constraint Index in the range of 1 to 12. Also contemplated herein as having a Constraint Index in the range of 1 to 12 and therefore within the scope of the defined novel class of highly siliceous zeolites are those zeolites which, when tested under two or more sets of conditions within the above-specified ranges of temperature and conversion, produce a value of the Constraint Index slightly less than 1, e.g. 0.9, or somewhat greater than 12, e.g. 14 or 15, with at least one other value within the 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 crystalline zeolite when identified by any combination of conditions within the testing definition set forth herein as having a Constraint Index in the range of 1 to 12 is intended to be included in the instant novel zeolite definition whether or not the same identical zeolite, when tested under other of the defined conditions, may give a Constraint Index value outside of the range of 1 to 12.

The novel class of zeolites defined herein is exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48, and other similar materials or hydrogen forms thereof.

ZSM-5 is described in greater detail in U.S. Patents No. 3,702,886 and Re 29,948. ZSM-11 is described in U.S. Patent No. 3,709,979. ZSM-12 is described in U.S. Patent No. 3,832,449. ZSM-23 is described in U.S. Patent No. 4,076,842. ZSM-35 is described in U.S. Patent No. 4,016,245 and ZSM-38 is described in U.S. Patent No. 4,046,859. ZSM-38 is described in U.S. Patent No. 4,046,859.

Although the zeolites may contain silica and alumina, it is recognized that the silica and alumina portions may be replaced in whole or in part with other oxides. For example GeO_2 is an art recognized substitute for SiO_2, and B_2O_3, Cr_2O_3, Fe_2O_3 and Ga_2O_3 are art recognized replacements for Al_2O_3. Accordingly the term zeolite as used herein shall connote not only materials containing silicon and, optionally, aluminium atoms in the crystalline lattice structure thereof, but also materials which contain suitable replacement atoms for silicon and/or aluminium. U.S. Patent Nos. 4,269,813; 4,327,236; 4,285,919 and 4,331,641 describe the preparation of boron-containing ZSM-5 zeolite in which boron is introduced in the crystalline lattice structure. Great Britain Patent Application No. GB 2,024,790 describes modification of ZSM-5 type crystalline materials by which boron, chromium, beryllium, titanium, vanadium, manganese, iron, cobalt, zinc, zirconium, rhodium, silver, tin and antimony have entered the crystalline lattice of the silica in place of silicon. Introduction of boron and various other metals into the lattice structure of ZSM-5 is also discussed in Great Britain Patent Application No. GB 2,033,358. In addition, alumina-silica zeolites may also contain such metals as phosphorous.

The conversion of synthesis gas in greater yield to the more desired valuable products of diesel fuel and heavier hydrocarbons is greatly enhanced by simultaneously employing the above-referred to crystalline aluminosilicate zeolites exemplified by ZSM-5 judiciously in a minor effective quantity, with a conventional Fischer-Tropsch catalyst.

To achieve the proper conditions contemplated by the invention, it is necessary to have a limited amount of zeolite activity associated with the disclosed catalyst system. Typically the operation is carried out with solid catalyst particles comprising Fischer-Tropsch synthesis catalyst and a fraction (f) of zeolite catalyst, with the zeolite activity being (alpha), and operating under conditions which produce (W) weights, of liquid product per weight of total solid catalyst charge, per hour, whereby these parameters are related by the condition that:

$$f . \alpha . W = A . n$$

A is a characteristic number, which depends on the temperature of operation, and which will be specified further below and n is a whole number or fraction thereof from 1 to 10. The zeolite activity alpha (α) is defined by its activity to crack *n*-hexane. Alpha is the value of the first order cracking rate constant for the particular sample relative to that of an equal volume of a standard amorphous silica-alumina catalyst, and measured at 538°C. The test has been described more fully in a paper by D. H. Olson, W. O. Haag, R. M. Lago, published in the Journal of Catalysis, Vol. 61, pp. 319-336, 1980 and in previous publications cited therein, the comments of which are incorporated in their entirety by reference. The desired alpha activity of the zeolite can be varied by synthesizing it with a required or specific silica to alumina ratio as shown in the above referenced publication. Lower alpha value zeolites can be obtained by steaming or by deactivation with partial cation exchange, e.g., potassium or sodium ions. Alpha values (activity) from 1 to 200 may be used. Preferred are values from 20 to 150.

The novel conversion of syngas, or synthesis gas, i.e., mixtures of gaseous carbon oxides with hydrogen or hydrogen donors to hydrocarbon mixtures and oxygenates, in accordance with the disclosed process is carried out at temperatures ranging from 190 to 300°C and more particularly from 220° to 280°C at gas hourly space velocities (GHSV), ranging from 250 to 20,000 and more desirably from 350 to 6,000, based on fresh feed and total catalyst volume. The rate of liquid product generation is typically between 0.5 and 5 weight/weight of catalyst charge/hr. Hydrogen to carbon oxides ratios can vary from 0.5:1 to 2:1 and more preferably are 1:1, pressures ranging from 3 to 70 atmospheres and more preferably from 10 to 35 atmospheres are employed. Any suitable Fischer-Tropsch feed (stream) may be used as long as it contains substantial amounts of syngas, i.e., hydrogen and carbon oxygenates such as CO and CO_2.

In the relationship outlined above, which characterizes the range of catalyst properties and operating conditions of this invention, the value of A will change or vary inversely with the average operating temperature approximately as follows:

Temperature, °C	*A*
190 to 225	150 μm
225 to 250	18 μm
250 to 300	2 to 3 μm

Since it is important to effect conversion of the heaviest fraction of wax, the catalyst particle size, zeolite crystal size will be preferably be as small as possible. Suitable zeolite crystalline size can vary from 0.01 to 1 μm (micrometer) and preferably from 0.02 to above 0.1 μm. Fluidized granule sizes thereof can vary from less than 0.1 mm to 1.0 mm. Preferred are sizes from 1.0 to 150 μm. This is particularly true for mechanical mixtures of the catalyst charge.

It is possible under proper circumstances and desirable to make a composite catalyst particle of both zeolite and metal-synthesis composition, with activities and relative amounts otherwise similar to the above descriptions.

Care must be taken that the process conditions are strictly adhered to or the resulting product will not be the desired predominantly heavier liquids. The use of the zeolite allows the synthesis to be carried out at lower temperatures than otherwise possible. The selection of a certain level of zeolite activity (alpha) is necessary to insure only a limited amount of activity, that is, just enough activity to prevent wax coating of the catalyst particles. The action of the catalytic materials assures operability at the lower temperature, while such lower temperature condition promotes a product distribution with significantly higher proportions of heavier liquids, such as diesel oil, than would be obtained at the temperature of the conventional synthesis in absence of zeolite catalyst.

Generally speaking, the modified catalyst system will contain up to 96 wt.% or preferably from 60 to 90% or more of the Fischer-Tropsch catalyst and from 2 to 20% of the zeolite catalyst depending, inter alia, upon operating parameters. However, the weight or volume ratio of F-T catalyst to zeolite can vary from 1-100 to 1 or 2 and preferably 30 to 1 to 5 to 1. Resultant yields of diesel oil will comprise at least 15-20 wt.% diesel oil based on the total liquid product produced. However, higher yields of 30% and up to 45% or more of diesel oil are possible if all factors are indeed maximized. The diesel oil produced will normally have an initial boiling point of 165°C and an end point of 400°C and preferably boiling between 210 and 350°C. Prior art methods generally produce 10%-12% or less of diesel oil, as disclosed in an article by M. E. Dry, Research Department, SASOL, Sasolburg, South Africa in Catalysis: Science and Technology, 1981, 1, 159-255, Anderson and Boudart, Eds.

It will be useful to use zeolite components which have been exposed to ion exchange with monovalent metals or alkali metals such as K, Na, Ce and Ru, in order to prevent further loss and migration of such metallic ions from, for example, iron-containing Fischer-Tropsch catalyst having minor amounts thereof. Potassium ion-exchange is preferred. The migration of potassium and other such metals away from the Fischer-Tropsch catalyst component to the zeolite can also be inhibited by providing the zeolite with cations which possess much higher affinities to, e.g., aluminium sites than does the potassium ion. This is accomplished by providing the zeolite component with multivalent ions that occupy most of the cationic exchange sites of aluminium. Thus the calcium form, or other alkaline earth metal ions are attractive examples. Exchange with rare earth metals such as lanthanum or cerium is also attractive.

The particle size and density differences between the particles of Fischer-Tropsch synthesis catalyst and those of the zeolite containing component can be favorable utilized in the fluid bed or entrained bed reaction system, to separate the two components to such an extent as to enable control of make-up rates individually.

The following examples illustrate without limiting the novel process of this invention.

Example 1

An iron-containing Fischer-Tropsch catalyst composition is operated in the Fischer-Tropsch synthesis mode at 230°C, using a CO/hydrogen ratio of 1:2, and a sufficient gas flow rate to generate 2 weights of liquid product per weight of catalyst per hour. The molecular weight distribution of the liquid product is determined by conventional liquid/vapor chromatography. The ratio of products above that corresponding to C_{16}^+ hydrocarbon waxes, and the amount of liquid below that molecular weight is determined.

Example 2

An iron-containing Fischer-Tropsch catalyst composition is mechanically mingled with ZSM-5 catalyst particles in proportion comprising 70% of the former and 15% of ZSM-5 zeolite of an alpha activity of 140. The combined material is charged to a reactor and operated in the Fischer-Tropsch synthesis mode at 230°C, using a hydrogen/CO ratio of 2:1, and a sufficient gas flow rate to generate 2 weights of liquid product per weight of catalyst per hour. The molecular weight distribution of the liquid product is determined by conventional liquid/vapor chromatography. The ratio of products above that corresponding to C_{16}^+ hydrocarbons to the amount of liquid below that molecular weight is determined. It was found to be appreciably lower than in the case of Example 1, and sufficiently low to avoid the sticking together of catalyst particles by C_{16}^+ hydrocarbon waxes. The value of $f\alpha$ W calculates to be 42.

Example 3

An iron-containing Fischer-Tropsch catalyst composition is mechanically mingled with ZSM-5 catalyst particles in proportion comprising 96% of the former and 2% of ZSM-5 zeolite of an alpha activity of 60. The combined material is charged to a reactor and operated in the Fischer-Tropsch synthesis mode at 270°C, using a hydrogen/CO ratio of 2:1, and a sufficient gas flow rate to generate 2 weights of liquid product per weight of catalyst per hour. The molecular weight distribution of the liquid product is determined by conventional liquid/vapor chromatography. The ratio of products above that corresponding to C_{16}^+ hydrocarbons, to the amount of liquid below that molecular weight is determined. This ratio was found to be significantly lower than in Example 1, and low enough to prevent the sticking of catalyst particles. The value of $f\alpha$ W calculates to be 2.4.

Example 4

An iron-containing Fischer-Tropsch catalyst composition is mechanically mingled with ZSM-5 catalyst particles in proportion comprising 50% of the former and 35% of ZSM-5 zeolite of an alpha activity of 140. The combined material is charged to a reactor and operated in the Fischer-Tropsch synthesis mode at 260°C, using a hydrogen/CO ratio of 2:1, and a sufficient gas flow rate to generate 2 weights of liquid product per weight of catalyst per hour. The molecular weight distribution of the liquid product is determined by conventional liquid/vapor chromatography. The ratio of products above that corresponding to C_{16}^+ hydrocarbons, to the amount of liquid below that molecular weight is determined. It was found to be significantly lower than in Example 1; but also, the amount of diesel boiling range product is significantly decreased at the expense of greater production of gasoline and gases. The calculated value of $F\alpha$ W in this case is about 100, and is greater than desired to maximize heavier hydrocarbon and diesel fuel production at this operating temperature.

The above-described exemplary material clearly illustrates that the novel Fischer-Tropsch process in accordance with the invention provides increased yields of diesel oil and heavier hydrocarbons. However, it is to be understood that the catalysts may not only be mixed so as to allow simultaneous contact with the feedstream but may also be arranged in any manner known to the art which will allow the zeolite catalyst to be downstream of the Fischer-Tropsch in the fluidized catalyst bed.

CLAIMS

1. A method for maximizing the production of diesel oil and heavier hydrocarbon oils from a suitable synthesis gas feed comprising operating a fluid mode Fischer-Tropsch synthesis process in the presence of a catalyst system comprising a major proportion of a Fischer-Tropsch synthesis catalyst modified with a minor proportion of an aluminosilicate zeolite catalyst wherein the fraction of zeolite catalyst used, zeolite activity and the amount of liquid product produced are controlled in accordance with the following equation:

$$f \,.\, \alpha \,.\, W = A \,.\, n$$

where f is the fraction of zeolite catalyst used, α is zeolite activity, W is the weight of liquid product per weight of total solid catalyst charge per hour, A is an average number which varies inversely with the operating temperature and n is a whole number or a fraction thereof from 1 to 10, thereby selectively converting or cracking sufficient waxy product to prevent adhesion between catalyst particles, so as to maintain catalyst fluidity and maximize diesel oil and heavier hydrocarbon yield.

2. The process of claim 1 wherein the liquid product contains at least 15 wt.% diesel oil based on the total weight of the product.

3. The process of claim 1 wherein the temperature varies from 190° to 300°C at a GHSV ranging from 250 to 20,000, W is between 0.5 and 5 weights/weight of catalyst charge/hour at pressures ranging from 3 to 70 atmospheres.

4. The process of claim 1 wherein the α value varies from about 1 to 200.

5. The process of claim 1 wherein the synthesis feed is simultaneously contacted by particles of Fischer-Tropsch and the zeolite catalyst.

6. The process of claim 1 wherein the zeolite catalyst is downstream of the Fischer-Tropsch catalyst.

7. The process of claim 1 wherein the major proportion varies from 60 to 96% and the minor proportion varies from 2 to 20%.

8. The process of claim 1 wherein the ratio of Fischer-Tropsch catalyst to zeolite catalyst varies from 100 to 1 to 1 to 2.

9. The process of claim 1 wherein A is 150 at a temperature of 190° to 225°C, 18 at 225° to 250°C and 2 to 3 at 250° to 300°C.

10. The process of claim 1 wherein the Fischer Tropsch synthesis catalyst is selected from iron, cobalt, ruthenium, thorium, rhodium, osmium, mixtures thereof, or suitable compounds thereof, or the metals or the suitable compounds thereof with minor amounts of K, Sn, P, W, rare earths, V, Mn or Mo.

11. The process of claim 1 wherein the zeolite catalyst is selected from ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48 or hydrogen forms thereof.

12. The process of claim 1 wherein the zeolite catalyst has a silica to alumina ratio of at least 12 and a constraint index of from 1 to 12.

13. The process of claim 12 wherein the zeolite has been ion exchanged with monovalent ions or with multivalent ions.

14. The process of claim 1 wherein the catalysts are moving in a fluidized or entrained bed.

15. The process of claim 1 wherein the synthesis gas feed contains hydrogen and carbon oxide or oxygenates in a ratio of from 0.5:1 to 2:1.

16. The process of claim 15 wherein the operating temperature is 230°C and the catalyst system comprises 70% Fischer-Tropsch catalyst, and 15% zeolite catalyst with an α value of 140.

17. The process of claim 16 wherein the value of $f\alpha W$ calculates to be about 42.

18. The process of claim 16 wherein the zeolite catalyst is ZSM-5.

19. The process of claim 16 wherein the catalysts are mechanically mingled.

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