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Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 188 872
A1**

12

EUROPEAN PATENT APPLICATION

21 Application number: 85307481.3

51 Int. Cl.4: **C07C 2/00** , C10G 3/00

22 Date of filing: 17.10.85

30 Priority: 13.12.84 US 681413

43 Date of publication of application:
30.07.86 Bulletin 86/31

84 Designated Contracting States:
BE DE FR GB IT NL

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54 **Process for upgrading fischer-tropsch olefins.**

57 In a process for converting an olefinic feedstock such as olefinic liquid product of Fischer-Tropsch synthesis, into distillate hydrocarbons over an acid zeolite oligomerization catalyst oligomerization is carried out in the presence of hydrogen to inhibit coke formation and thereby reduce catalyst aging.

EP 0 188 872 A1

PROCESS FOR UPGRADING FISCHER-TROPSCH OLEFINS

This invention relates to a continuous process for the manufacture of distillate range hydrocarbon fuels, and more particularly, it provides a process for converting olefinic feedstocks containing alkenes and oxygenates at elevated temperature and pressure into distillate products over zeolite-containing oligomerization catalysts.

The conversion of lower olefins into gasoline and/or distillate products is described in U.S. Patents 3,960,978 and 4,021,502, gaseous olefins in the range of ethylene to pentene, either alone or together with paraffins, being converted into an olefinic gasoline blending stock by contacting the olefins with a bed of a ZSM-5 type zeolite-containing catalyst. U.S. Patents 4,150,062, 4,211,640 and 4,227,992 describe similar processes for converting olefins into gasoline and/or distillate components. U.S. Patent 4,456,779 describes operating conditions for the Mobil Olefins to Gasoline/Distillate (MOGD) process for selective conversion of C₃⁺ olefins into mainly aliphatic hydrocarbons. Typically, the process recycles gas or liquid hydrocarbons from a high-temperature, high-pressure separator downstream of the catalyst bed, into the reaction zone where additional olefins are converted into gasoline and distillate products. If the reaction of the olefins in converting them into distillate and gasoline is allowed to progress in the catalyst stream without any measures taken to prevent the accumulation of heat, the reaction becomes so exothermically accelerated as to result in high temperatures and the production of undesired products.

In the conversion of olefins into heavier hydrocarbons by catalytic oligomerization using a medium pore, shape selective, acid crystalline zeolite, such as ZSM-5 type zeolite, process conditions can be varied to favor the formation of either gasoline or distillate range products. At moderate temperatures and relatively high pressures, the conversion conditions favor aliphatic distillate range product having a normal boiling point of at least 165°C. Lower olefinic feedstocks containing C₂-C₆ alkenes may be converted; however, the distillate mode conditions do not convert a major fraction of ethylene. One source of olefinic feedstocks of interest for conversion into heavier fuel products is the intermediate olefin-rich naphtha or light oil obtained as a liquid product from Fischer-Tropsch conversion of synthesis gas. A typical feedstock consists essentially of C₂-C₆ mono-olefins with a minor amount of coproduced oxygenate from Fischer-Tropsch synthesis. These feedstocks are suitable for upgrading into more valuable heavier hydrocarbon; however, the organic oxygenated content may cause catalyst aging due to formation of coke during the conversion process.

During the course of a single catalyst cycle, reactor temperatures must be raised to maintain the desired conversion of olefins into gasoline and/or distillate, and to maintain desired product liquid quality. Beyond a certain temperature, however, these objectives cannot be met and the catalyst must be regenerated. It is desirable to minimize the frequency of regeneration by decreasing the temperature aging rate. This reduces the inconvenience and cost of frequent regenerations, and may also extend the ultimate life of the catalyst, which experiences permanent activity loss over the course of many regenerations.

The present invention seeks to provide a continuous process devised for upgrading synthol intermediate olefins to a valuable heavy distillate fuel product.

According to the invention, a continuous process is provided for converting a feedstock mixture comprising a major amount of lower olefins and a minor amount of oxygenated hydrocarbons into higher hydrocarbons comprising distillate product, including the step of contacting the feedstock in the presence of hydrogen with an oligomerization catalyst comprising a shape selective, medium pore, acid zeolite at an elevated temperature and pressure to convert olefins into heavier hydrocarbons. Preferably, the conversion is followed by reducing pressure on the effluent to flash volatile components into a vapor phase and recover a heavy liquid stream, condensing a major portion of the vapor phase by cooling under pressure to recover a liquid intermediate olefin stream and recover condensed water by-product from oxygenate conversion into hydrocarbons, and fractionating the heavy liquid stream from the flashed reactor effluent to recover a heavy distillate hydrocarbon product stream. This technique is particularly useful in extending catalyst life by inhibiting coke formation on the catalyst due to oxygenate conversion.

A recycle stream containing olefinic boiling range components may be further converted into distillate product. In conjunction with reactor operating conditions, the recycle composition and rate determine the distillate product boiling range and properties such as viscosity.

The invention is described below in greater detail by way of example only with reference to the accompanying drawings, in which

FIG. 1 is a process flow sheet showing the major unit operations and process streams;

FIG. 2 is a schematic representation of a fixed bed reactor system and product separation system; and

FIG. 3 is a plot of reactor temperature against stream time for comparative runs.

The amount of cofed hydrogen sufficient to inhibit coke formation may vary considerably depending upon a number of factors. Feedstocks containing trace amounts of oxygenates can be mixed with a relatively small amount, for example, as little as 1 mole %, of H₂. Increased oxygenate content will require a greater amount of hydrogen. It is preferred to operate the process with a minor amount of hydrogen, usually less than 50 mole %, in order to avoid diluting the olefinic feed components. It is known that pure olefins, such as propene, can be oligomerized over HZSM-5 without substantially modifying the reaction except for the partial pressure. The presence of hydrogenation components such as Ni and Pt can interfere with the desired process steps and should be avoided in the presence of hydrogen.

The oxygenate content of the Fischer-Tropsch light oil can be controlled by pretreatment of the feedstock by extraction or the like. If the same oxygenate impurities are fed to the unit under steady state conditions, the water recovery rate can indicate the average oxygenate content, and this is an indirect measure of the potential for coke formation inherent in the feedstock. Thus, hydrogen feed rate can be regulated as a function of feedstock oxygenate content, usually with a preset minimum H₂ feed to ensure adequate protection in the event of oxygenate surges.

The preferred oligomerization catalysts include crystalline aluminosilicate zeolites having a silica to alumina ratio of at least 12, a constraint index of 1 to 12 and acid cracking activity (alpha value) greater than 120, preferably 160 to 200. Representative of the ZSM-5 type zeolites are ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35 and ZSM-38. ZSM-5 is described in U.S. Patents 3,702,886 and Re. 29,948 and ZSM-11 is described in U.S. Patent 3,709,979. U.S. Patent 3,832,449 describes ZSM-12; U.S. Patent 4,076,842 describes ZSM-23; U.S. Patent 4,016,245 describes ZSM-35 and U.S. Patent 4,046,839 describes ZSM-38. A suitable catalyst for fixed bed operations comprises HZSM-5 zeolite with an alumina binder in the form of 1 to 5 cylindrical extrudates. Other pentasil catalysts which may be used in one or more reactor stages include a variety of medium pore (approximately 5 to 9 Angstroms) siliceous materials such as borosilicates, ferrosilicates, and/or aluminosilicates described in U.S. Patents 4,414,423, 4,417,086, 4,417,087 and 4,417,088.

The zeolite catalyzes a number of known reactions in addition to the oligomerization-interpolymerization reactions which are favored in producing the C₁₀-C₂₀ or higher molecular weight aliphatic materials useful as distillate fuel. At higher temperatures, acid cracking tends to diminish product yield. Brønsted acid sites are provided by strong aluminosilicates and it is preferred to maintain a high effective alpha value, although certain metal cation-exchanged zeolites may be useful.

Catalyst aging can be caused by accumulation of very heavy product and/or process coke. It is known that relatively pure olefin feedstocks cause only minor deposition of non-strippable coke. The heavy hydrocarbonaceous deposits accumulated by non-oxygenated hydrocarbon can be stripped by high temperature gases. Harder process coke which results from dehydration and conversion reactions involving alcohols, ketones, aldehydes, and other oxygenates, cannot be adequately rejuvenated or regenerated by stripping alone, and oxidative reactivation is required to restore the catalyst to substantially full activity.

The flowsheet diagram of Figure 1 shows the relationship of the process to the preceding syngas conversion and prerefractionation unit operations, depicting the further conversion of the C₅-C₈ rich olefinic intermediate, phase separation and recycle. Heavy hydrocarbons are recovered by fractionation and sent to a conventional hydrotreating unit for product finishing.

In the process of the present invention, olefinic gasoline is separated from reactor effluent in an efficient manner to provide a recycle stream rich in C₅ to C₉ hydrocarbons and having only minor amounts of C₄⁻ compounds or distillate range product. The gasoline recycle stream is obtained by a phase separation technique in which the reactor effluent stream is cooled to condense heavy hydrocarbons, especially distillate materials, which are recovered in a liquid stream. These aspects are shown in greater detail in Figure 2 and in the following description.

Referring to Figure 2 of the drawings, an olefinic feedstock in conduit 1 is normally liquid and is brought to process pressure by means of pump 10. Pressurized hydrogen gas is supplied via conduit 5 and combined with the feedstock, which is preheated by passing sequentially through a series of heat exchangers 11, 12 and 13 and reactant effluent exchangers 14C, B and A, and furnace 16 prior to entering the catalytic reactor system 20.

A typical distillate mode first stage reactor system 20 is shown. A multi-reactor system is employed with inter-zone cooling, whereby the reaction exotherm can be carefully controlled to prevent excessive temperature above the nor-

mal moderate range of about 230° to 325°. While process pressure may be maintained over a wide range, usually from about 2800 to over 10,000 kPa, the preferred pressure is about 4000 to 7000 kPa. The feedstock is heated to reaction temperature and carried sequentially through a series of catalyst beds 20A, B and C in which at least a portion of the olefin content is converted into heavier distillate constituents. Advantageously, the maximum temperature differential across any one reactor is about 30°C and the space velocity (LHSV based on olefin feed) is about 0.5 to 1.5. The heat exchangers 12A and 12B provide inter-reactor cooling and 12C reduces the effluent to flashing temperature. Control valve 25, operatively connected between the reactor section 20 and a phase separator unit 30 provides means for reducing the process pressure, thereby vaporizing volatile components of the effluent stream, such as unreacted lighter hydrocarbons (for example, C₅-C₈ alkenes) and water. The separator may be a vertical cylindrical vessel having a hooded tangential inlet to effect separation of the flashed effluent mixture. A demister pad 31 prevents substantial liquid entrainment and a major amount of the overhead vapor is withdrawn through conduits 34 and 36, cooled indirectly by incoming feedstock in exchangers 13 and 11 and passed through air cooler 38 to condense the lighter and intermediate range hydrocarbons in the separator vapor phase along with unreacted hydrogen and byproduct water from oxygenate conversion. Separator tank 42 has an overhead gas conduit 40 for removing a hydrogen-rich stream and separates a water phase, which is withdrawn from the system through boot 44 and outlet 45. Condensed hydrocarbons provide essentially all of the liquid olefinic recycle stream and are passed through filter 46 and pump means 48 prior to combination with feedstock in conduit 49.

It is understood that design modification can be made to provide for recovery and recycle of hydrogen. For instance, vapor stream 40 may be further cooled in a heat exchanger to condense at least a portion of the hydrocarbon for recovery in an additional phase separator (not shown). Recovered hydrogen-rich gas can be compressed, purified and recycled to the reactor system along with makeup hydrogen 5. Condensed liquids from the optional final separation unit can be fed via line 37 to debutanizer 50.

Liquid hydrocarbons rich in distillate are recovered from phase separator 30 at flashing pressure, preferably about 1100 to 1500 kPa and passed via conduit 33 to debutanizer fractionation tower 50 at a lower stage therein where the heavy liquid contacts rising vapor from reboiler section 51 to vaporize dissolved lighter hydrocarbons, especially C₄⁻ hydrocarbons present in the feedstock or generated during conversion. The debutanizer overhead stream 52 may be cooled to produce reflux 54 and recovered as LPG byproduct through conduit 55 from accumulator 56.

The amount of recycle can be varied according to requirements. During steady state operation at design conditions, a minor amount (for example, 7-8%) of separator overhead vapor from line 34 may be taken as a slipstream through conduit 37 and sent directly to the debutanizer tower 50 at an intermediate stage. Light hydrocarbons and byproduct water are withdrawn with the tower overhead stream 52 and heavier hydrocarbons containing gasoline and/or distillate range hydrocarbons are sent along with the debutanizer bottoms stream 58 to product splitter 60 where the heavier hydrocarbons are fractionated to provide a condensed gasoline product 61 and condensed reflux 52. Light gas from separator 56 is rich in H₂ and C₂ compo-

nents. This off-gas may be used as fuel gas, or the hydrogen may be recovered by a hydrogen purification unit (not shown) and recycled under pressure, as described above.

Splitter tower 60 has a furnace-fired reboiler section 64 and the refined heavy distillate product is recovered through conduit 66, and cooled by incoming feedstock in exchanger 12 and in cooler 68. Advantageously, the distillate-rich liquid phase is fractionated to provide a major product stream consisting essentially of 154°C+ aliphatic hydrocarbons comprising a major amount of C₁₀-C₂₀ aliphatic hydrocarbons. This product may then be hydrotreated to provide a heavy distillate product.

There are several advantages to the process design. Usually the intermediate liquid recycle consists essentially of C₅+ hydrocarbons, with minor amounts of C₄- components. This recycle material has a relatively high heat capacity and provides a good heat sink without diminishing feedstock olefin partial pressure and thereby maintaining a high olefin partial pressure at reactor inlet. The distillate product quality is readily altered by changing the average molecular weight of recycled olefins. By increasing temperature in the separator units, a heavier distillate product with regulated viscosity is obtained, and the recycled portion is further upgraded to heavier product by further reaction. The liquid recycle is economically repressurized by pumping, which requires

modest power consumption. The debutanizer is operable at about 1000 kPa to condense all overhead without refrigeration, thus providing energy efficiency in obtaining the LPG byproduct. The product splitter tower can be operated at atmospheric pressure, thus holding the bottoms temperature to less than 273°C to provide raw distillate product stability.

A typical distillate mode oligomerization operation is conducted over a fixed bed of HZSM-5/alumina extrudate catalyst using the techniques described in U.S. Patents 4,456,779 and 4,433,185. Reactor sequencing and catalyst regeneration are known in the art.

Feedstock may be derived from synthesis gas conversion product made according to a commercial Fischer-Tropsch process (SASOL), described in U.S. Patent 4,111,792. Typically, such materials have an oxygenated hydrocarbon content of about 0.5 to 10 weight percent. A C₂-C₆ (82.5 weight %) olefin fractionation cut containing coproduced alcohol, ester, aldehyde, and/or ketone oxygenates is water washed to remove excess oxygenates and reduce their amount to less than 1 weight percent. The oligomerization feedstock properties for a preferred embodiment are set forth in Table I.

TABLE I

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FEED PROPERTIES

<u>Hydrocarbon Component</u>	<u>Weight Percent</u>
C ₂	0.1
Propene	11.6
Other C ₃	2.1
Butenes	24.5
Butanes	4.0
Pentenes	7.1
Pentanes	4.7
Hexenes	19.3
Hexanes	3.8
C ₇ ⁺	2.8
Dienes,	nil
Sulfur	nil
Nitrogen	nil
Oxygenates	0.6

CATALYST

65 weight% HZSM-5 (crystal size 1 mm)
 35 weight% Al₂O₃
 alpha value approximately 180

The following Examples illustrate the invention.

Example 1

The above feedstock is upgraded by reaction over ZSM-5 zeolite under conditions sufficient to convert at least 95% of the butenes and, with recycle, to produce at least 70 weight % distillate range product having an average viscosity of 3 centistokes. The process is run at 5600 kPa total pressure. The recycle is composed of C₅ to 230°C hydrocarbons separated from the reactor effluent and returned to the reactor at a volumetric rate of 2 parts recycle

per part of fresh feed. The average weight hourly space velocity is about 1 based on parts of fresh feed per part of catalyst. In one run, the feedstock plus recycle is co-fed with hydrogen (about 6 mole%) and in the comparative example hydrogen is omitted and an inert diluent (N₂) added. The effect of hydrogen addition on distillate properties is shown in Table II.

TABLE II

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PRODUCT PROPERTIES

P_{H_2} (partial pressure, kPa)	0	345
P_{N_2}	480	0
P_{Total} (kPa)	5620	5620

230°C+ Distillate Properties

Density, g/cc @ 15°C	0.8091	0.8044
Viscosity, centistokes	3.45	3.34
Distillation, °C		
10 weight% vaporized	247	239
30 "	261	256
50 "	278	276
70 "	301	302
90 "	343	344

During each of the continuous runs, the catalyst bed temperature was increased to maintain conversion and product quality. The catalyst aging rate was reduced by about 40% by addition of H_2 , as shown graphically in Fig 3.

Example 2

The procedure of Example 1 is repeated, except that the oxygenate content of the feedstock is about 2 weight %. Similar results are obtained in a 40-day continuous run, and the addition of hydrogen lowers the average aging rate to about 1.3°C/day.

Co-feeding hydrogen to the reactor reduces the start of cycle temperature and reduces the amount of aging. The scope of this concept is not limited to aging caused solely by oxygenate compounds. Aging may be caused by other contaminants or due to more severe operating conditions.

Claims

1. A continuous process for converting a feedstock mixture comprising a major amount of olefins and a minor amount of oxygenated hydrocarbons into higher hydrocarbons including distillate product, comprising:

contacting the diluted feedstock in the presence of hydrogen with an oligomerization catalyst comprising a shape selective, medium pore, acid zeolite at an elevated temperature and pressure to convert olefins into heavier hydrocarbons.

2. A process according to Claim 1, comprising the further steps of

reducing pressure on the oligomerization effluent to flash volatile components into a vapor phase and recover a heavy liquid stream from a phase separator;

30 condensing a major portion of the vapor phase by cooling under pressure to recover a liquid intermediate olefinic stream and to recover condensed water by-product from oxygenate conversion into hydrocarbons;

35 fractionating the heavy liquid stream from the flashed oligomerization effluent to recover a distillate hydrocarbon product stream; and

40 combining olefinic feedstock with a pressurized liquid diluent stream comprising a major fraction of the intermediate olefinic stream.

45 3. A process according to Claim 2, wherein the feedstock is combined with the olefinic recycle stream in a ratio of at least 2 moles of recycle per mole of feedstock olefin and contacted with a fixed bed of catalyst comprising an acid aluminosilicate zeolite having a constraint index of 1 to 12, at a temperature of 230 to 325°C and a pressure of 4000 to 7000 kPa, to convert a major amount of feedstock olefins.

50 4. A process according to Claim 2 or Claim 3, wherein the distillate-rich liquid stream is fractionated to provide a major product stream consisting essentially of 154°C+ fraction comprising a major amount of C_{10} - C_{20} aliphatic hydrocarbons.

55 5. A process according to any one of Claims 1 to 4, wherein the oligomerization catalyst comprises a ZSM-5 type zeolite and is essentially free of hydrogenation components.

60 6. A process according to Claim 5, wherein the zeolite has an acid cracking value of at least 120.

65 7. A process according to any one of Claims 1 to 6, wherein the feedstock is the product of Fischer-Tropsch

synthesis.

8. A process according to any one of Claims 1 to 7 wherein the hydrogen is present in an amount sufficient to inhibit coke formation on the oligomerization catalyst.

9. A process according to Claim 8, wherein the hydrogen is present in an amount substantially proportional to the ox-

xygenated hydrocarbon content of the feedstock mixture.

10. A process according to Claim 9, wherein the hydrogen is present in an amount comprising 1 to 50 mole percent of the feedstock mixture.

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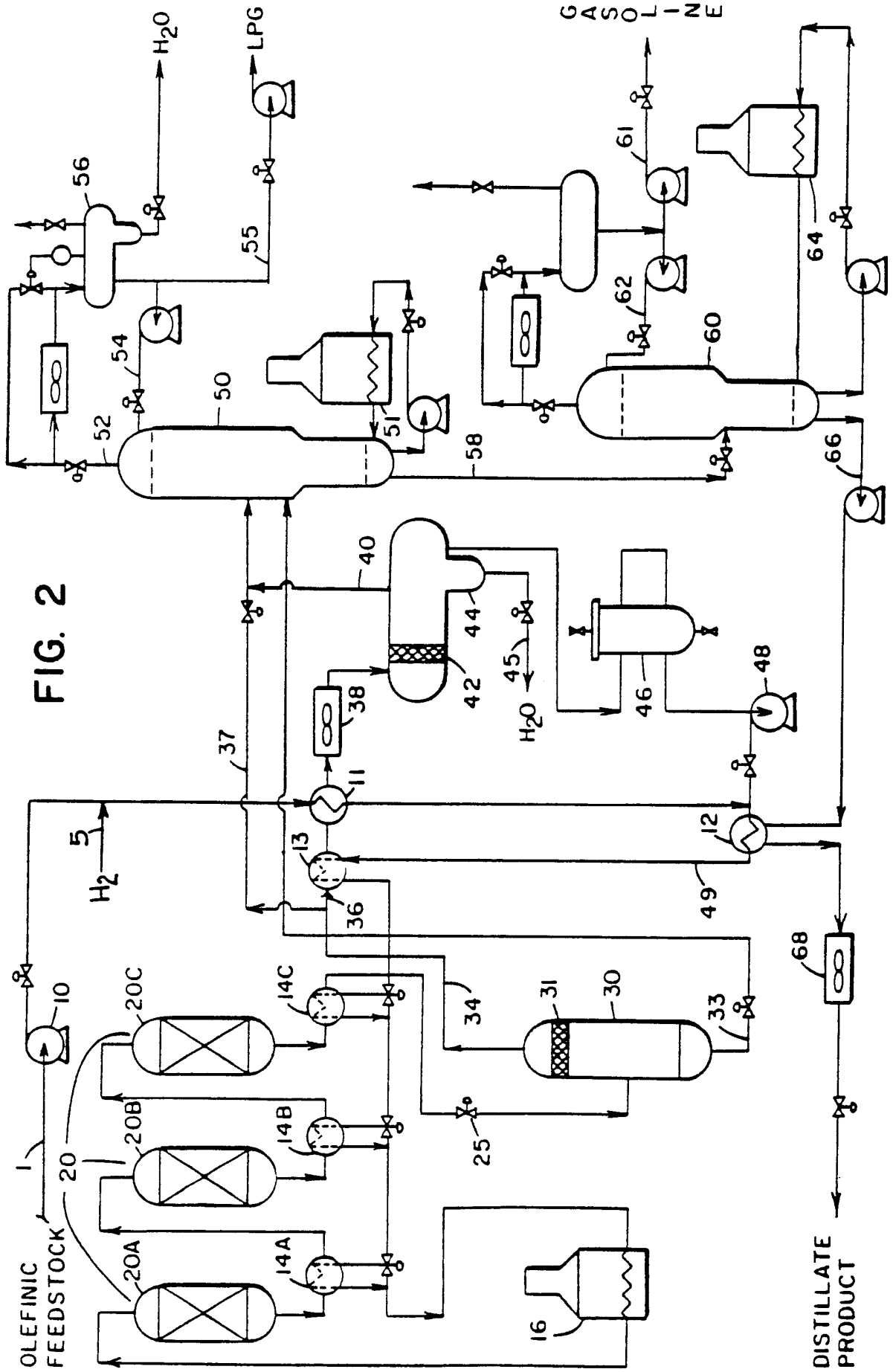


FIG. 2

FIG. 1

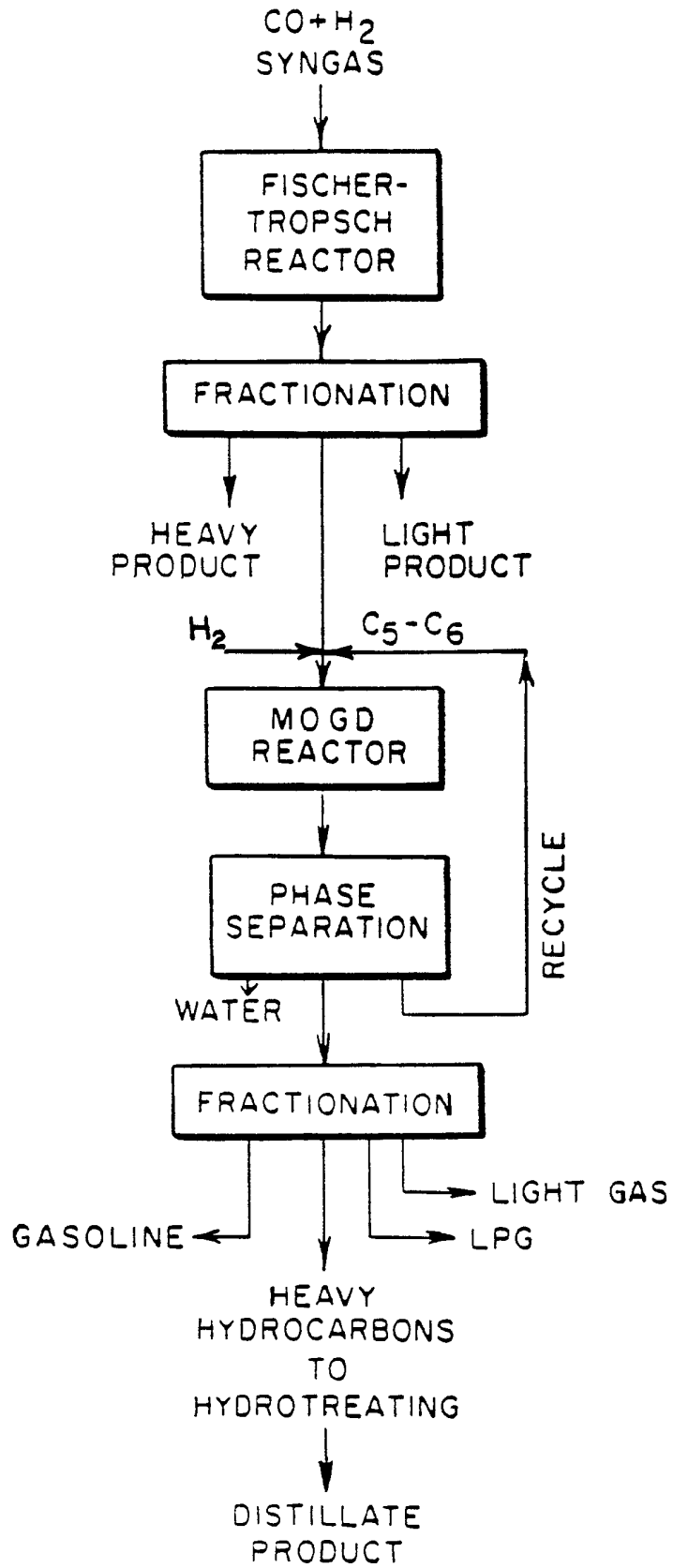
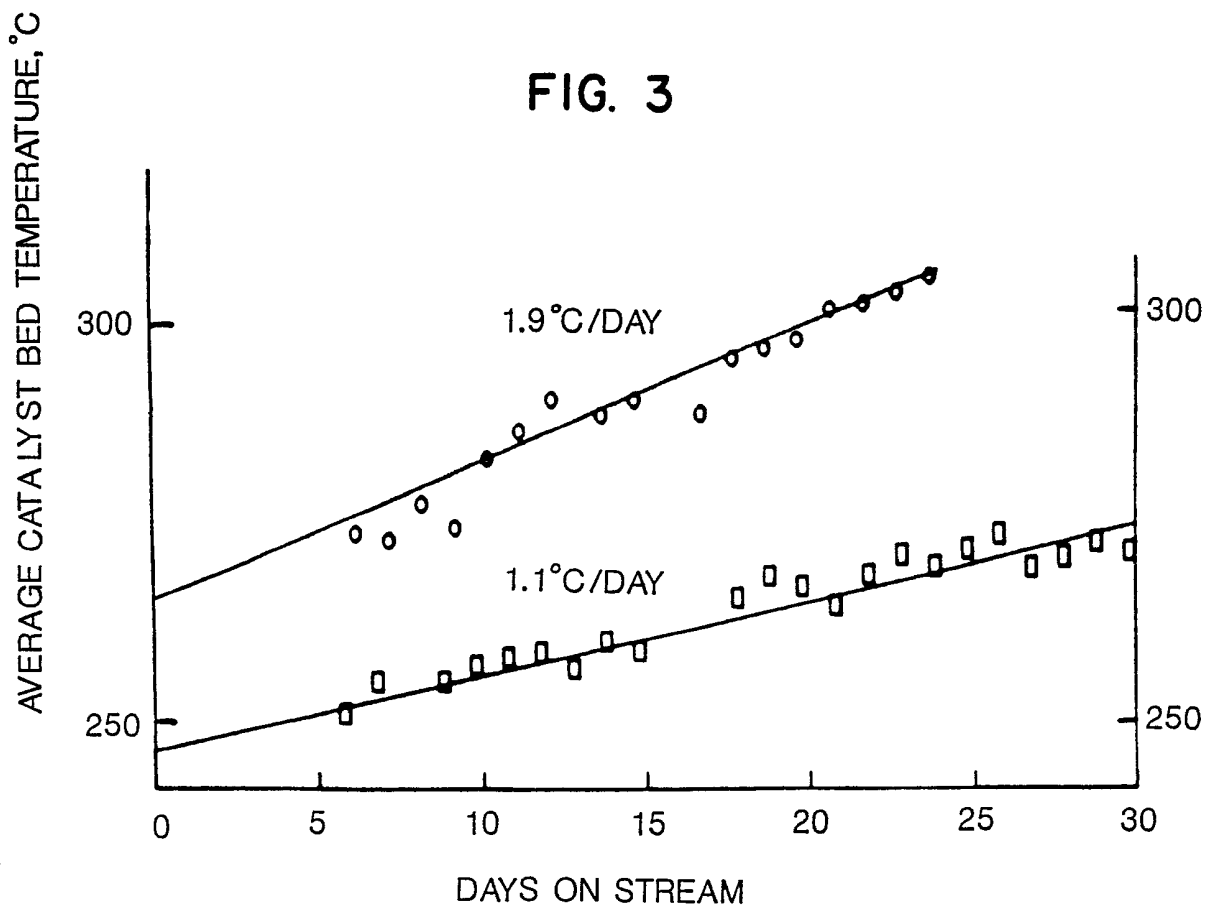


FIG. 3



○ NO HYDROGEN PRESENT

□ HYDROGEN PARTIAL PRESSURE 345 kPa



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,X	US-A-4 544 792 (SMITH et al.) * Claims *	1-10	C 07 C 2/00 C 10 G 3/00
P,X	--- US-A-4 520 215 (OWEN et al.) * Claims *	1-5	
A	--- US-A-4 126 644 (CAESAR et al.)		
A	--- US-A-4 430 516 (LA PIERRE et al.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 2/00 C 10 G 31/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25-04-1986	Examiner VAN GEYT J.J.A.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			