PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^{6} **:**
C07C 1/04, C10G 2/00

A1

(11) International Publication Number: **WO 98/19979**

(43) International Publication Date: 14 May 1998 (14.05.98)

(21) International Application Number: PCT/US97/19722

(22) International Filing Date: 30 October 1997 (30.10.97)

(30) Priority Data:
08/744,032 5 November 1996 (05.11.96) US

(71) Applicant: SYNTROLEUM CORPORATION [US/US]; Suite 1000, 400 South Boston, Tulsa, OK 74103 (US).

(72) Inventor: BEER, Gary, L.; 3301 Jomar Drive, Plano, TX 75075 (US).

(74) Agent: FELGER, Thomas, R.; Baker & Botts, L.L.P., 2001 Ross Avenue, Dallas, TX 75201-2980 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: GAS CONVERSION PROCESS USING A CHAIN-LIMITING REACTOR

(57) Abstract

A Fischer-Tropsch process for converting syngas to a hydrocarbon product wherein the product has a desired chain length, e.g. diesel. The syngas is passed through a fluidized-bed of catalyst in a chain-limiting reactor until the chain length of the hydrocarbon being absorbed on said catalyst reaches a chain length which is substantially equal to the chain length of the desired hydrocarbon product. This "saturated" portion of the catalyst is then removed from the reactor and is replaced with fresh catalyst. The "saturated" catalyst is regenerated and recycled to the reactor.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

GAS CONVERSION PROCESS USING A CHAIN-LIMITING REACTOR

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a process for converting gases to liquids and in one of its aspects relates to a process for converting "syngas" (e.g. hydrogen and carbon monoxide) to a hydrocarbon liquid (e.g. gasoline, distillates, etc.) by passing the syngas in contact with a catalyst in a chain-limiting reactor wherein the catalyst is removed from the reactor and replaced with "clean" catalyst before undesirable, long-chain hydrocarbons are formed within the reactor.

BACKGROUND OF THE INVENTION

The desirability to convert light, hydrocarbon gases (e.g. natural gas) to liquids (e.g. methanol, gasolines, diesel, other distillates, etc.) has long been recognized. Probably the best known process for carrying out this type of conversion is one wherein natural gas is first flowed through an Autothermal Reformer, e.g. a partial oxidation reformer, to convert the natural gas to a synthesis gas ("syngas", i.e. a gas comprised of carbon monoxide (CO) and hydrogen (H_2)). The syngas is then fed to a Fischer-Tropsch synthesis type of reactor which is loaded with an appropriate catalyst which, in turn, converts the syngas to a desired product (e.g. methanol, gasolines, diesel, other distillates, etc.) depending on the catalyst and the operating conditions within the reactor. Such processes are well-known in the industry; for examples of Fischer-Tropsch processes of this type, see U.S. Patents 1,798,288; 2,500,533; 2,552,308; 4,579,985; and 4,973,453.

Fischer-Tropsch ("F-T") synthesis proceeds by adding one carbon atom at a time to a growing chain which, in turn, is adsorbed onto an active metal catalytic site. The chain length of the product is a function of the probability of the chain continuing to grow versus the probability of the product desorbing from the catalyst without further growth. Different catalyst formulations have various probabilities for growth, leading to differing chain lengths being produced by each catalyst. Operating conditions can also affect the probability of growth and thereby dictate chain length.

In most commonly-practiced F-T synthesis operations, the distribution of different chain lengths roughly follows a polymerization model called "Shulz-Flory" (e.g. see THE FISCHER-TROPSCH SYNTHESIS, R.B. Anderson, Academic Press, Inc., N.Y., 1984, pps. 186-187. This distribution indicates that there is an equal probability of growth regardless of the desired chain length. This constrains the product distribution significantly in any particular F-T synthesis since when using preferred catalysts for producing a desired hydrocarbon liquid product (e.g. diesel), large quantities of a lesser desired hydrocarbon product (e.g. methane) will also be produced which have to then be disposed of.

For example, if a catalyst is used which will maximize a gasoline range product (e.g. C_7 to C_9), then a large amount of less valuable gas (e.g. C_1 to C_4) will also be produced in the same operation. If a distillate product (e.g. C_{20+}) is desired, then the required catalyst will also produce a large fraction of heavy waxes (e.g. C_{35+}) which, in turn, must then be "cracked" back to the desired product. Accordingly, it can be seen that it would be desirable to limit the chain growth of hydrocarbons on the catalyst during a particular operation to that of the desired product so that substantially all of the product being produced in the F-T operation will be that which is desired, e.g. diesel.

One technique which has been proposed for limiting chain growth on a catalyst during a F-T operation is disclosed in U.S. Patent 2,247,087 wherein a fixed bed reaction mass, i.e. catalyst, is constantly or periodically treated to remove longer-chain hydrocarbons (e.g. paraffin) from the surface of the catalyst as the hydrocarbons are being formed to thereby limit the chain length of the hydrocarbons within the reactor to that of the more desirable hydrocarbon products. This is done in the disclosed process by using solvents to remove the long-chained hydrocarbons (i.e. paraffin) from the catalyst. The reference also points out that control of chain length may also be further effected by changing (a) the operating pressures and/or temperatures within the reactor; and (b) the composition of the feed gas being fed to the fixed bed, reactive mass.

SUMMARY OF THE INVENTION

The present invention provides a Fischer-Tropsch process for converting syngas to a desired hydrocarbon product wherein the product has a desired chain length, e.g. diesel. Basically, the process involves passing the syngas through a bed of catalyst to convert the syngas to the desired product until at least a portion of the catalyst reaches a saturated state with "saturated state" being defined as when the hydrocarbon which is being absorbed on said catalyst reaches a chain length which is substantially equal to the chain length of the desired product.

When the chain length of the hydrocarbon being absorbed on the catalyst substantially reaches that of the desired hydrocarbon, the saturated portion of the catalyst is removed and replaced with fresh or unsaturated catalyst. The saturated catalyst is then "regenerated" by passing a fluid e.g. steam, over the catalyst to thereby remove the absorded hydrocarbon therefrom. The saturated catalyst is replaced with unsaturated catalyst at a rate substantially equal to the rate at which said saturated catalyst is removed. By timing the contact between the syngas and the catalyst, the growth of the hydrocarbon chain is limited to that of the desired hydrocarbon product.

More particularly, the present invention is directed to a Fischer-Tropsch process for converting syngas to a desired hydrocarbon product having a desired chain length wherein the process is carried out in a chain-limiting reactor. The syngas is passed through a fluidized bed of catalyst in the chain-limiting reactor. Fresh or unsaturated catalyst is carried by the syngas into the bottom of the reactor where it forces the catalyst in the fluidized bed upward therein.

The catalyst remains in contact with the syngas as it rises within the reactor and the length of the chain of the hydrocarbon being absorbed on the catalyst continues to grow. The retention time of the catalyst in the reactor (i.e. the time it takes for fresh catalyst entering into the bottom of the reactor to rise to the takeout point at the top) is such that the hydrocarbon chain on the catalyst will grow as the catalyst moves toward the top of the reactor and will attain its maximum desired length (i.e. substantially equal to the chain length of the desired hydrocarbon product) as the catalyst reaches the takeout point.

As the catalyst reaches its "saturated state", the saturated portion of the catalyst exits the reactor and is transferred to a regeneration vessel where a regenerating fluid, e.g. stripping gas, steam, etc., is passed over the catalyst to remove the hydrocarbon product therefrom. The regenerated or now unsaturated catalyst can then be recycled to the reactor. Preferably, the chain-limiting reactor is of the type known as "a fluidized-bed" reactor or a "circulating fluidized-bed" reactor. In order to maintain the integrity of the fluidized-bed of catalyst within the reactor, the chain-limiting reactor is operated at a temperature and pressure at which said hydrocarbon product remains a vapor while in said reactor. This vaporized hydrocarbon product is removed from the reactor and can easily be condensed to the desired liquid product, e.g. diesel.

BRIEF DESCRIPTION OF THE DRAWINGS

The actual construction, operation, and apparent advantages of the present invention will be better understood by referring to the drawings which are not necessarily to scale and in which like numerals refer to like parts and in which:

FIGURE 1 is a schematic representation of a fluidized-bed, chain-limiting reactor system for carrying out a process in accordance with the present invention;

FIGURE 2 is a graph showing the probability of the growth of hydrocarbon chains verses the selectivity of a desired product to be formed during an F-T process; and

FIGURE 3 is a schematic representation of another embodiment of a chain-limiting reactor which can be used in carrying out the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring more particularly to the drawings, FIGURE 1 discloses a schematic diagram of a fluidized bed system S which can be used in carrying out a gas-to-liquid conversion process in accordance with the present invention. System S is comprised of a reactor vessel 1 of a type commonly used in certain, standard fluidized-bed reactor-type operations, e.g. fluid catalytic cracking refinery processes. It should be recognized that vessel 1 can take other configurations without departing from the present invention.

A feed gas ("syngas", i.e. a gas comprised of carbon monoxide (CO) and hydrogen (H_2)) is fed through supply line 2 into the bottom of vessel 1 and flows upward through fluidized bed which is comprised of a Fischer-Tropsch synthesis catalyst. As used herein, "synthesis catalyst" is any appropriate catalytic material which will convert the particular feed gas flowing into vessel 1 into a particular desired product. That is, the particular catalyst will depend on the feed gas and the particular product to be formed. For example, where the feed gas is syngas and the product is methanol, a typical synthesis catalyst can be copper on alumina, e.g. BASR copper catalyst type S3-85. For longer-chain hydrocarbon products, cobalt-based Fischer-Tropsch catalyst can be used e.g., see U.S. Patents 4,579,985; 4,579,986; 4,587,008; and 4,640,766.

Synthesis catalyst is in the form of loose, unconsolidated granular particles of various diameters, e.g. less than 1 micron to 2.5 inches, whereby the catalyst particles comprise a "fluidized-bed" as used and understood in the art. Catalyst bed 4 as shown in FIGURE 1 is an example of a fluidized bed. For a good general discussion of typical fluidized-bed systems of this general type, see CHEMICAL ENGINEERS' HANDBOOK, J.H. Perry, 4th Edition, McGraw-Hill Book Co., pps 20-42 to 20-53.

The feed gas, e.g. syngas, flows upward through catalyst bed 4 at a superficial velocity. "Superficial velocity" is understood in this art and is based on the flow of gas through reactor vessel 1 when the vessel is empty and is that velocity at which the upflowing gases will enlarge the spaces between the particles in catalyst bed 4 to a point where no stable arrangements between individual particles can exist and the particles will vibrate or circulate in a semi-stable arrangement; hence the velocity at which catalyst bed 4 becomes a "fluidized-bed".

Exothermic heat which is generated by the catalytic reaction is extracted from the reaction zone (i.e. catalyst bed 4) to control the operating temperature within reactor 1. This can be done in several ways; for example as shown, a heat exchanger 5 which has a plurality of vertical tubes 5a is positioned within and extends substantially through catalyst bed 4. A heat-conducting fluid, e.g. water, enters through pipe 6 and flows through vertical tubes 5a to pick up heat from the reaction mass 4. The heated fluid, e.g. steam, exits exchanger 5 through pipe 7 for disposal, e.g. power generation, recycling, etc. By controlling the flow rate of the heat-conducting fluid, a desired, average operating temperature can be maintained within reactor 1.

As the feed gas flows upward through fluidized catalyst bed 4, the feedgas, e.g. syngas, is converted to product (e.g. diesel) upon contact with particles in catalyst bed 4. In accordance with the present invention, it is desirable to maintain reactor 1 at operating conditions, i.e. temperature and pressure, which will insure that not only substantial amounts of the feed gas will be converted to the desired hydrocarbon product, but also that the converted hydrocarbon product, itself, will remain in its vapor phase until it exits from reactor 1.

Of course, the actual operating temperatures and pressures during any particular conversion operation will depend upon the composition of the feed gas, desired product, the particular catalyst used, etc.. For example, if the feed gas is to be converted to diesel, the temperature in the reactor will likely be from about 350°F. to about 550° F. and the pressure can range from about 15 to 600 psia depending on the composition of the feed gas, the particular catalyst used, etc. The reason that it is desirable to maintain the desired product in its vapor phase while in the reactor is that the presence of any substantial amount of liquids within reactor 1 will adversely affect the integrity of the fluidized catalyst bed 4, possibly to the point of making the process inoperable. As will be understood, the vaporized product (e.g. diesel) flows out of reactor 1 through outlet 10 and on to further processing equipment (not shown) where it is readily condensed into the desired liquid hydrocarbon product. It should be understood that any fines or particles of catalyst bed 4 which is carried by the vapor through outlet 10 can be separated from the product (e.g. by a hydrocyclone or the like, not shown) for reuse in the process.

As will be understood by those skilled in this art, the Fischer-Tropsch process within reactor 1 converts the feed gas ("syngas", i.e. a gas comprised of carbon monoxide (CO) and hydrogen (H_2)) into the desired hydrocarbon product by adding one carbon atom at a time to a growing chain which is being adsorbed onto an active site on the particles of catalyst bed 4. The chain length of the desired product then becomes a function of the probability of the chain continuing to grow versus the probability of desorbing with no further growth. Catalyst formulations which are used to form a desired hydrocarbon product have various probabilities for growth (see FIGURE 2) leading to different chain lengths being produced by each particular catalyst.

This phenomena significantly affects the ability a catalyst to form substantially only one product during a particular Fischer-Tropsch process. That is, where a particular catalyst is used to form a desired product such as diesel, large amounts of undesirable (i.e. less valuable) light-hydrocarbon gases (e.g. methane) are also inherently formed during the process which have to be handled or otherwise disposed of. Likewise, in a F-T process where a different catalyst is used to form a heavier, distillate product a large fraction of heavy waxes will also be produced along with the desired distillates. For a good discussion of the probability of chain growth as it relates to product selectivity, see "Chemicals Produced in a Commercial Fischer-Tropsch Process", INDUSTRIAL CHEMICALS VIA C_1 PROCESSES, Chapter 2, M.E. Dry, American Chemical Society Journal, Vol. 328, 1987.

In accordance with the present invention, the residence time of each catalyst particle within reactor 1 is controlled so as to limit the growth of the hydrocarbon chain which is adsorbed onto the surface of each catalyst particle to correspond substantially with the length of the hydrocarbon chain of the desired product. That is, catalyst particles remain in reactor 1 until the particles become "saturated", i.e. the length of the hydrocarbon chain being absorbed onto the surface of the particles is substantially equal to the length of the chain of the desired hydrocarbon product. At this point, the "saturated" catalyst particles are removed from reactor 1 and "regenerate" by removing the adsorbed hydrocarbons therefrom.

In the present invention, limiting the chain length of the hydrocarbon product produced by F-T synthesis may be accomplished by continuously supplying "fresh" catalyst into the bottom of reactor 1 and removing "saturated" catalyst at the top of catalyst bed 4. As shown, the fresh catalyst is mixed with and is carried into the reactor 1 by the feed gas which enters through inlet 2. The catalyst, as it enters reactor 1, forces the catalyst already in catalyst bed 4 upward in the reactor so that the top of catalyst bed 4 effectively remains at a level adjacent catalyst outlet 9. Since the catalyst is withdrawn from the reactor at basically the same rate as catalyst is being added, the depth of catalyst bed 4 remains substantially constant.

Since the length of the chain on the surface of the catalyst will begin to grow as it first comes into contact with the feed gas and will continue to grow as the catalyst particles move upward within catalyst bed 4, the hydrocarbon chain formed on the catalyst will be substantially at its maximum length when the catalyst particles reach the top of catalyst bed 4. Therefore, by timing the arrival of the catalyst particles at outlet 9 to coincide with the desired maximum growth of the hydrocarbon chain absorbed thereon, the length of the chain on the catalyst particles exiting from reactor 1 will always be substantially equal to or less than the length of the chain of the hydrocarbon product which is desired to be formed during the process. This allows the majority, if not substantially all, of the hydrocarbon product being formed during the operation to be that which is desired.

The catalyst particles are withdrawn through outlet 9 and supplied to column 15 where they are treated to "regenerate" the catalyst particles by removing the hydrocarbons which have been adsorbed thereon. This can be done by passing a regenerating fluid or sweep gas (e.g. steam, feed gas) into the column 15 through pipe 20. The sweep gas passes over the catalyst particles to desorb the hydrocarbons which, in turn, are then carried by the sweep gas out of the top of column 15 through outlet 16. Any fines or particles of catalyst which are carried out of column 15 in the sweep gas/desorbed hydrocarbon stream preferably flows through hydrocyclone 17 or the like from which the separated catalyst is returned to column 15 though line 19 and passes the gas/hydrocarbons onto storage or other use through line 18.

It should be noted that the hydrocarbons desorbed from the catalyst in column 15 will have basically the same chain length as the desired hydrocarbon product so that the stream in line 18 can be processed and used accordingly. The "regenerated" catalyst is removed from the bottom of column 15 and is passed through valve 21 to storage hopper 22 from which it is then fed through valve 23 back into feed gas inlet line 2 to again be used in the process.

The actual retention time which each catalyst particle will remain in reactor 1 will obviously depend on the particular catalyst being used, the design of the reactor, the operating conditions within the reactor, the hydrocarbon product to be formed, etc., all of which can be determined experimentally once all of the process parameters and the configuration of the reactor are known.

FIGURE 3 illustrates a slightly different, circulating fluidized-bed, chain-limiting reactor system S_a which can be used in carrying out the present invention. System S_a is similar to system S of FIGURE 1 except the catalyst is continuously circulated through reactor vessel 1a at a rate whereby the length of the hydrocarbon chain on the catalyst reaches it maximum growth as the catalyst exits reactor 1a through outlet conduct 10a. Reactor vessel 1a has a heat exchanger 5a therein to control the temperature of the reaction as described above.

The feed gas (e.g. syngas) flows through inlet 2a and through the catalyst bed 4a within reactor 1a. Further, the feed gas picks up "regenerated" catalyst from line 24a and carries it into reactor 1a where the catalyst forces the existing catalyst in bed 4a upward whereby the catalyst at the top of the bed is carried through conduit 10a along with the desired product. Again, the catalyst is replaced at the bottom of reactor 1a at substantially the same rate as that at which the catalyst at the top of reactor 1a is being removed. The "residence time" which the catalyst remains active in reactor 1a is timed so that the hydrocarbon chain on the catalyst will substantially reach its maximum length (i.e. length of desired product) as it exits from reactor 1a.

The produced hydrocarbon gas (i.e. converted feed gas) carries the "saturated" catalyst through conduit 10a and into column 15a. The produced hydrocarbon gas (e.g. vaporized gasoline) and the catalyst separate or disengage within the wide upper section of column 15a. The hydrocarbon product flows through product outlet 16a which includes hydrocyclones 17a or the like which separate any fines or particles of catalyst from the hydrocarbon product and return them back into column 15a. A "regenerating fluid" (e.g. sweep gas such as steam) flows from pipe 20 upward through the saturated catalyst in the lower section of column 15a to "desorb" the produced hydrocarbons from the catalyst.

The sweep gas and the desorbed hydrocarbons, which are basically the same as the desired hydrocarbon product, are removed through product outlet 16a for further processing. The "regenerated" catalyst falls to the bottom of column 15a where it is returned to inlet 2a through control valve 23a for reuse in the process.

WHAT IS CLAIMED IS:

1. A Fischer-Tropsch process carried out in a chain-limiting reactor for converting syngas to a desired hydrocarbon product having a desired chain length, said process comprising:

passing said syngas through a fluidized bed of catalyst in said chain-limiting reactor to convert said syngas to said hydrocarbon product;

operating said reactor at temperature and pressure at which said hydrocarbon product remains in its vapor phase while in said reactor;

removing said hydrocarbon product while in its vapor phase from said chain-limiting reactor;

continuously removing catalyst from said chain-limiting reactor as the chain length of any hydrocarbon product absorbed on said catalyst reaches said desired chain length for said hydrocarbon product; and

continuously supplying fresh catalyst in said chain-limiting reactor at the same rate as that at which said catalyst is removed.

2. The Fischer-Tropsch process of Claim 1 including regenerating said catalyst after it is removed from said chain-limiting reactor to remove said absorbed hydrocarbon product therefrom.

3. The Fischer-Tropsch process of claim 2 wherein said fresh catalyst comprises the catalyst which has been removed from said chain-limiting reactor after it has been regenerated.

4. The Fischer-Tropsch process of claim 1 wherein said catalyst is removed from said chain-limiting reactor along with said vaporized hydrocarbon product.

5. The Fischer-Tropsch process of claim 4 including separating said vaporized hydrocarbon product from said removed catalyst;

regenerating said catalyst to remove any of said hydrocarbon product which was absorbed thereon; and

returning said regenerated catalyst to said chain-limiting reactor.

6. The Fischer-Tropsch process of claim 5 including combining said vaporized hydrocarbon product and said hydrocarbon product removed from said catalyst.

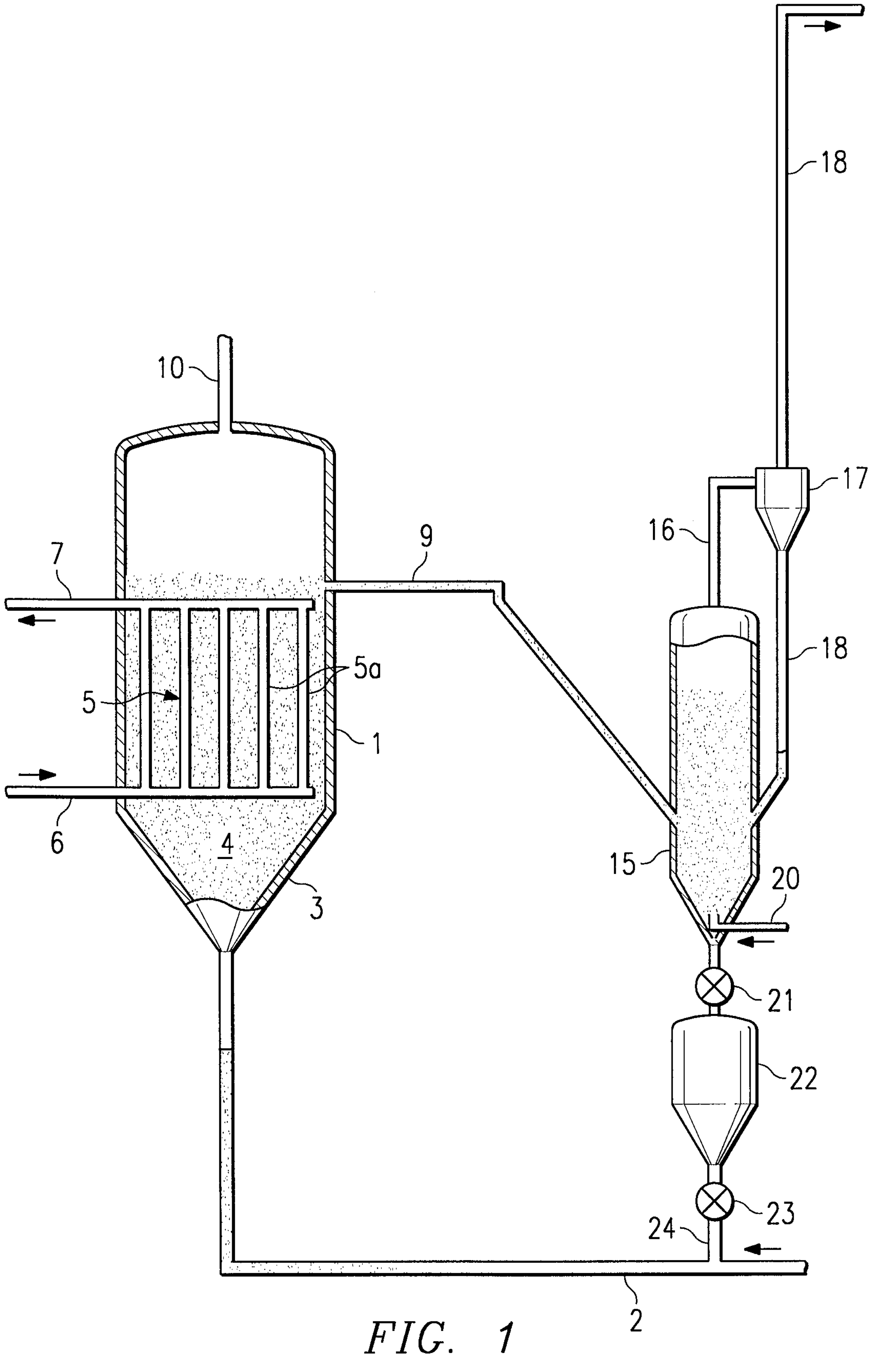

FIG. 1

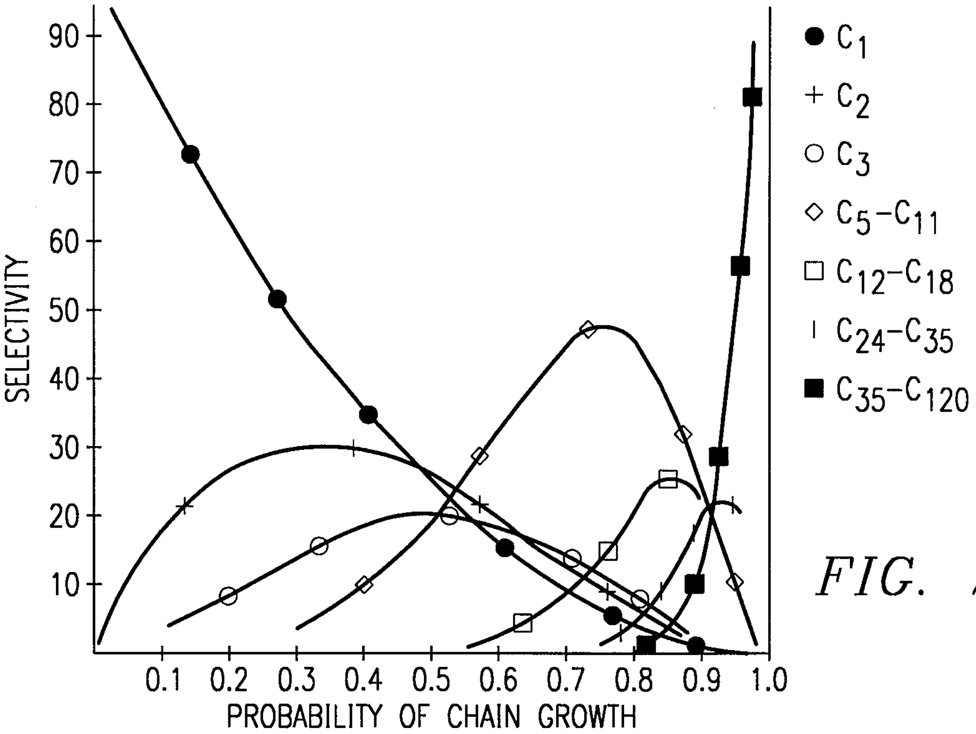
SELECTIVITY
90
80
70
60
50
40
30
20
10
0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
PROBABILITY OF CHAIN GROWTH
● C_1
+ C_2
○ C_3
◇ C_5-C_{11}
□ $C_{12}-C_{18}$
| $C_{24}-C_{35}$
■ $C_{35}-C_{120}$

FIG. 2

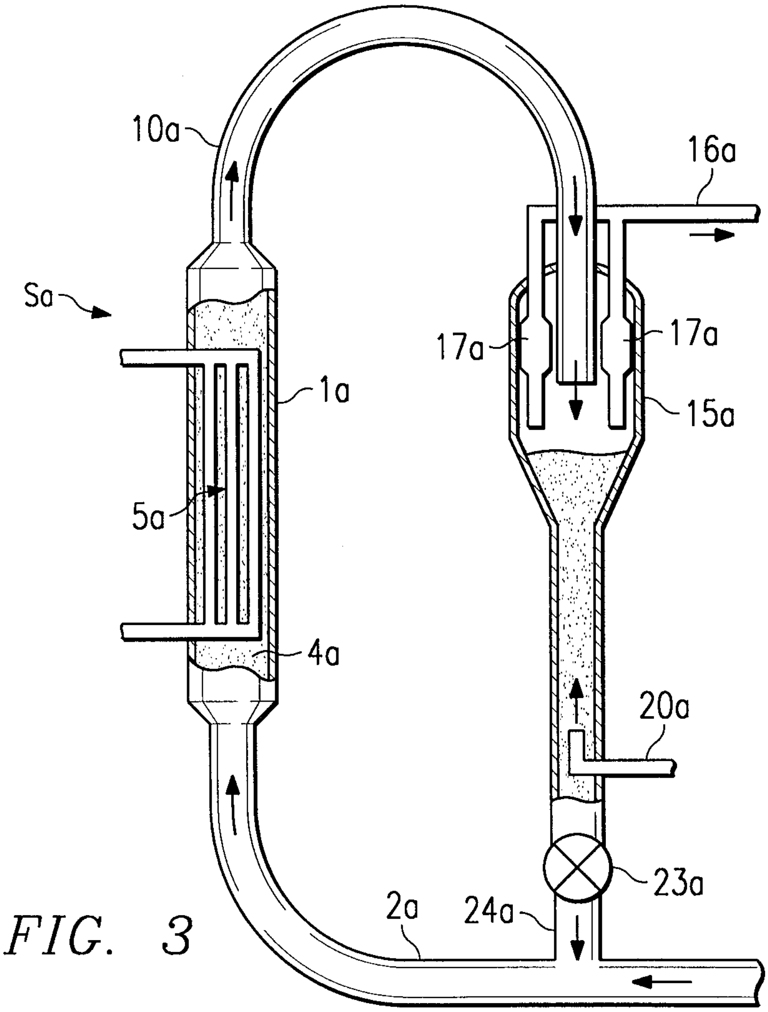
10a
16a
Sa
17a
17a
1a
15a
5a
4a
20a
23a
2a
24a

FIG. 3

INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/US 97/19722

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C1/04 C10G2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BE 414 019 A (I.G. FARBENINDUSTRIE) 31 March 1936 see page 1 - page 2 ---	1-6
A	FR 922 493 A (STANDARD OIL DEVELOPMENT COMPANY) 10 June 1947 see claims -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

1

Date of the actual completion of the international search 12 February 1998	Date of mailing of the international search report 25/02/1998
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Van Geyt, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/US 97/19722

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
BE 414019 A		NONE	
FR 922493 A	24-06-47	NONE	