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PATENT SPECIFICATION

635,219

Date of Application and filing Complete Specification: Aug. 28, 1946

No. 25782/45.

Application made in United States of America on Sept. 10, 1945.

Complete Specification Published: April 5, 1950.

2638

Index at acceptance:—Class 2(iii), B1g.

COMPLETE SPECIFICATION

Improvements in or relating to Synthesis of Hydrocarbons

We, PHILLIPS PETROLEUM COMPANY, a Corporation organized under the laws of

gas comprises a mixture of about 2 mols. of hydrogen per mol. of carbon

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ERRATUM

SPECIFICATION No. 635,219.

In the heading on page 1, *for* "No. 25782/45" *read* "No. 25782/46"

THE PATENT OFFICE,
1*st October*, 1950.

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hydrocarbons and oxygenated compounds. The formation of hydrocarbons having more than one carbon atom per molecule, especially those hydrocarbons boiling within the gasoline range, is favoured by relatively low pressures and low temperatures.

In general, the syntheses of hydrocarbons by the hydrogenation of carbon monoxide is accomplished in the presence of a metal chosen from Group VIII of the Periodic Table as a catalyst at pressures below about 500 pounds per square inch gauge and at temperatures below about 350° C. The synthesis feed

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$$CO + 3H_2 = CH_4 + H_2O_{(g)};\ \Delta F^\circ = -51{,}300 + 56.2T$$
$$2CO + 5H_2 = C_2H_6 + 2H_2O_{(g)};\ \Delta F^\circ = -90{,}400 + 117.4T$$
$$6CO + 12H_2 = n-C_6H_{12(g)} + 6H_2O_{(g)};\ \Delta F^\circ = -211{,}400 + 316.3T$$
$$6CO + 13H_2 = n-C_6H_{14(g)} + 6H_2O_{(g)};\ \Delta F^\circ = -241{,}300 + 350.2T$$
$$8CO + 17H_2 = n-C_8H_{18(g)} + 8H_2O_{(g)};\ \Delta F^\circ = -317{,}500 + 466.6T$$

[*Price* 2/-]

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COMPLETE SPECIFICATION

Improvements in or relating to Synthesis of Hydrocarbons

We, PHILLIPS PETROLEUM COMPANY, a Corporation organized under the laws of the State of Delaware, United States of America, of Bartlesville, Oklahoma, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the synthesis of hydrocarbons. In one aspect this invention relates to the conversion of hydrogen and carbon monoxide into hydrocarbons. In still another aspect this invention relates to the synthesis of normally liquid hydrocarbons by the interaction of hydrogen and carbon monoxide in the presence of a synthesis catalyst.

It has been known for some time that hydrogen and carbon monoxide may be made to react exothermically in the presence of certain catalysts and under specific reaction conditions to form hydrocarbons and oxygenated compounds. The formation of hydrocarbons having more than one carbon atom per molecule, especially those hydrocarbons boiling within the gasoline range, is favoured by relatively low pressures and low temperatures.

In general, the syntheses of hydrocarbons by the hydrogenation of carbon monoxide is accomplished in the presence of a metal chosen from Group VIII of the Periodic Table as a catalyst at pressures below about 500 pounds per square inch gauge and at temperatures below about 350° C. The synthesis feed gas comprises a mixture of about 2 mols. of hydrogen per mol. of carbon monoxide, and is prepared by the catalytic conversion of natural gas, steam and carbon dioxide.

It has previously been proposed to conduct the syntheses reaction in a liquid medium containing, or trickling over, the catalyst. In this way temperature control is simplified. The liquid medium used may be partially volatile under the conditions of operation and is normally of hydrocarbonaceous nature and may advantageously consist of the oils obtained in a previous synthesis.

It is highly desirable to produce a product of predominantly normally liquid hydrocarbons, especially a hydrocarbon fraction boiling within the gasoline range. Whether a normally gaseous, liquid or solid hydrocarbon is produced depends to some extent upon the reaction conditions, especially temperature, which are used to effect the synthesis.

The application of thermodynamic principles to the hydrogenation of carbon monoxide indicates the feasibility of producing those hydrocarbons boiling within the gasoline range. The approximate linear free energy-temperature relations for the synthesis of methane, ethane, normal hexene, normal hexane, and normal octane, are illustrated by the following over-all equations for reactions occurring in the gas phase with nickel or cobalt catalysts. These equations are represented graphically in "The Chemistry of Petroleum Derivatives" by Carleton Ellis, Vol. II; 1934, page 1226.

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[*Price 2/-*]

The production of hydrocarbons from carbon monoxide and hydrogen is favoured thermodynamically, as is evident from the large negative values of the standard free energy change for the over-all reactions. In the series, methane, ethane, hexene, normal hexane, and normal octane, the free energy change becomes more negative with the size of the molecule so that the formation of higher members of the series is quite feasible. At about 300° C., and atmospheric pressure, it should be possible to obtain any of the paraffin hydrocarbons by reduction of carbon monoxide in the presence of appropriate catalysts. The validity of this conclusion has been confirmed by the isolation and identification of some of the reaction products which included practically all the members of the aliphatic series from ethane to hectopentacontane ($C_{150}H_{302}$).

An object of this invention is to increase the yield of hydrocarbons having more than one carbon atom per molecule in the hydrogenation of carbon monoxide.

Another object is to synthetically produce normally liquid hydrocarbons boiling within the gasoline range by the interaction of hydrogen and carbon monoxide in the presence of a suitable synthesis catalyst.

The present invention comprises a process for the synthesis of hydrocarbons having more than one carbon atom in the molecule which comprises reacting hydrogen with carbon monoxide at a temperature such that hydrocarbons are produced and at a pressure of from 15 to 2000 p.s.i.g. in the presence of a catalyst comprising a metal from Group VIII of the periodic table and introducing into the reaction zone a hydrocarbon fraction boiling between 25° and 200° C. and comprising straight and/or branched chain saturated or unsaturated hydrocarbons, said hydrocarbon fraction being wholly in the vapour phase under the conditions of the reaction.

The hydrocarbon introduced into the reaction zone comprises a hydrocarbon having not less than 5 carbon atoms per molecule and not more than 12 carbon atoms per molecule. Preferably, the hydrocarbon is an unsaturated aliphatic hydrocarbon, such as a hexene, a heptene, or an octene. The hydrocarbon may be introduced alone or in admixture with other hydrocarbons. When the hydrocarbon is introduced as a hydrocarbon mixture, preferably the mixture comprises a predominantly olefinic hydrocarbon fraction boiling within the range between 25 and 200° C., such as a fraction obtained from a refinery cracking process.

Although the hydrocarbon may be introduced into the reaction zone as a liquid, conditions of temperature and pressure are maintained in the reaction zone such that all of the hydrocarbon is volatilized and passes through the reaction zone as a vapour with the hydrogen and carbon monoxide. In some instances it may be desirable to introduce the hydrocarbon into the reaction zone directly as a vapour.

The hydrocarbon may be injected into the reaction zone separately or in admixture with the hydrogen and carbon monoxide. Multipoint injection of the hydrocarbon separately into the reaction zone along the path of flow of the reactants is within the scope of this invention. The manner of introducing the hydrocarbon or mixture of hydrocarbons into the reaction zone is not considered limiting, but the hydrocarbon is present in the reaction zone as a vapour rather than as a liquid.

The exact mechanism of the reactions involved by the presence of the hydrocarbon is not definitely known. However, when using an unsaturated hydrocarbon, the unsaturated hydrocarbon probably reacts with the normally gaseous hydrocarbons formed in the reaction zone to produce heavier hydrocarbons as is evidenced by the increased yield of heavier hydrocarbons. The reaction may be that of alkylation, or conjunct polymerization, or both. Nevertheless, the presence of a relatively heavy hydrocarbon in the reaction zone, whether saturated or unsaturated, results in a substantially increased yield of heavier hydrocarbons, especially normally liquid hydrocarbons. The addition of such a hydrocarbon to the synthesis reaction does not consume any substantial amount of hydrogen, and thus the consumption of hydrogen is not increased above that consumed by the normal synthesis reaction without the addition of the hydrocarbon.

An effluent is withdrawn from the reaction zone and products of the process separated therefrom.

It has been found that the reintroduction of an intermediate fraction separated from the total hydrocarbon product of the synthesis reaction is particularly effective in increasing the yield of normally liquid hydrocarbons. The preferred embodiment of this invention comprises reacting hydrogen and carbon monoxide in the reaction zone with a suitable synthesis catalyst comprising a metal of Group VIII of the periodic table under a pressure of from 15 to 2000 p.s.i.g. and at a temperature such that the hydrocarbons having more than one carbon atom per molecule are produced, withdrawing an effluent from the reaction zone, and separating and recycling to the reaction zone at least a portion of the hydrocarbon product boiling within the range between 25 and 200° C.

In general, that portion of the hydrocarbon product which boils within the gasoline range is recycled to the reaction zone. Such a fraction ranges from C_5 hydrocarbons to C_8 or C_9 or even C_{10} hydrocarbons. From 5 to 7 parts by weight of recycle to 10 parts of total hydrocarbon product is recycled.

Since it is preferred to introduce a hydrocarbon mixture which has a substantial proportion of unsaturated hydrocarbons therein, the synthesis reaction is carried out in such a manner that the proportion of unsaturated hydrocarbons formed by the initial interaction of hydrogen and carbon monoxide is relatively high. The proportion of unsaturated hydrocarbons is influenced by the catalyst and by the ratio of hydrogen to carbon monoxide.

The relative tendency to form unsaturated hydrocarbons in the presence of various synthesis catalysts is shown in Table I below:

TABLE I.

Catalyst	
Sintered Iron	Unsaturated
Iron	↑
Nickel	↑ ↓
Cobalt-Thoria	↓
Ruthenium	Saturated

Sintered iron or an iron catalyst is preferred as the synthesis catalyst to be used in effecting the formation of hydrocarbons from hydrogen and carbon monoxide when additional hydrocarbons are introduced into the reaction zone.

Upon use the catalyst may decrease in activity as the result of the deposition of carbonaceous deposits thereon. Regeneration of the catalyst may be achieved in the conventional manner, such as by treatment with hydrogen at elevated temperatures.

A molar ratio of hydrogen to carbon monoxide between 3 to 1 and about 1 to 1 is used in effecting the synthesis reaction. However, since a decrease in the amount of hydrogen present in the synthesis reaction increases the tendency for the formation of unsaturated hydrocarbons, a molar ratio of hydrogen to carbon monoxide between about 3 to 2 and about 1 to 1 is preferred. When the feed mixture contains a ratio of hydrogen to carbon monoxide within the above ranges, this ratio remains substantially constant throughout the reaction. The recycle or introduction of a hydrocarbon fraction containing unsaturated hydrocarbons does not consume appreciable amounts of hydrogen and thus does not effect the hydrogen to carbon monoxide ratio.

A space velocity between 80 and 400 volumes of reactants per volume of catalyst per hour is adequate for effecting the synthesis reaction. Preferably, a space velocity between 100 and 200 is used but when using a sintered iron catalyst a space velocity of fresh reactants as high as 300 to 400 may be used with a recycle ratio of total effluent of about 100:1. The recycle or introduction of a normally liquid hydrocarbon fraction into the reaction zone does not appreciably change the space velocity. For example, using a space velocity of about 100, the recycle of a fraction as previously described will increase the space velocity to only about 102.

Table II below shows preferred temperatures and pressures for various catalysts which may be used in accordance with this invention.

TABLE II.

PREFERRED RANGES OF OPERATION OF SOME COMMON CATALYSTS FOR THE PRODUCTION OF SYNTHETIC HYDROCARBONS

	Temperature ° C.		Pressure, p.s.i.g.	
Catalyst	Broad Range	Pref. Range	Broad Range	Pref. Range
1 Cobalt-Thoria	180—250	190—210	15—500	100
2 Iron-Alkali and/or Copper	210—280	230—260	15—500	75—300
3 Sintered Iron	265—350	310—330	15—500	220—300
4 Ruthenium	180—250	190—210	1000—2000	1200—1500
5 Nickel-Thoria	175—220	190—210	15—100	15—50
6 Nickel-Manganese-Alumina	175—220	190—210	15—100	15—50
7 Cobalt	175—220	180—200	15—500	100

Another modification of the present invention comprises separating a hydrocarbon product boiling above about 200° C. from the synthesis process and cracking the same under known conditions, either thermally or catalytically. The cracked hydrocarbon fraction boiling between 25° and 200° C. is then recycled to the hydrocarbon synthesis reaction zone to promote the formation of normally liquid hydrocarbons. In this modification, substantially all of the hydrocarbon products of the synthesis process are utilized and an increased yield of normally liquid hydrocarbons is realized.

In some instances, depending on operating conditions, the catalyst used, and the composition of the recycle fraction, the normally liquid hydrocarbon product may contain undesirable unsaturated hydrocarbons. Under such circumstances the hydrocarbon product may be hydrogenated in the conventional manner to produce a more saturated hydrocarbon product.

The accompanying drawing diagrammatically represents apparatus for a typical process for the synthesis of hydrocarbons embodying the present invention.

In order that this invention may be more clearly understood and its applicability realized, a brief description of a process embodying features of the present invention will be illustrated. Natural gas containing methane, steam and carbon dioxide obtained from suitable sources are introduced into reactor 8 through lines 5, 6 and 7, respectively. Hydrogen and carbon monoxide are formed in reactor 8 in the presence of a suitable catalyst, such as nickel, at approximately atmospheric pressure and at a temperature between about 700 and about 800° C. The effluent from reactor 8 contains hydrogen and carbon monoxide in a molar ratio of about 2:1, and about 0.5 to about 1.0 mol. per cent. impurities, such as sulphur.

From reactor 8, the effluent passes to sulphur removal unit 12 by line 9 and through cooler 11. Both inorganic and organic sulphur are removed from the effluent in unit 12 by conventional methods known in the art. Inorganic sulphur may be removed by solvent extraction with an amine solution. Organic sulphur compounds are decomposed in the presence of a suitable catalyst, such as a copper oxide-lead chromate combination, at an elevated temperature of about 400° C. The resulting hydrogen sulphide from the decomposition is removed by solvent extraction. The purified effluent of hydrogen and carbon monoxide is then passed to heater 14 by line 13 and thence to reactor 16 by line 15.

In reactor 16 hydrocarbons are synthesized under reaction conditions similar to those previously described and in the presence of a suitable catalyst. A hydrocarbon fraction boiling between 25° C. and 200° C. is introduced into reactor 16 through lines 17, 18 and 19. This hydrocarbon fraction may be obtained from various sources; preferably, however, the fraction is obtained by separating a portion of the hydrocarbon product of the process and recycling the same to reactor 16 through lines 54 and 17.

From reactor 16 an effluent containing hydrocarbons is passed to cooler 22 via line 21 where partial condensation is effected and the condensation is collected in accumulator 23 and discharged therefrom through line 24. A portion of the effluent may be recycled to reactor 16 via line 20, if desired. This condensate comprises heavy hydrocarbons and waxes. The temperature of the effluent gases leaving reactor 16 is about 200° C.

and cooling the gases to about 150° C. is sufficient to accomplish the degree of partial condensation desired in accumulator 23. Uncondensed gases from accumulator 23 are passed to cooling tower 27 by line 28 wherein gases are condensed by a spray of water which cools them to about 25° C. Water and liquid hydrocarbons are withdrawn from tower 27 through line 29 and are passed to settler 31 for a liquid phase separation between hydrocarbons and water.

Uncondensed gases leave settler 31 through line 32 and pass to mineral seal oil absorber 33. Recovery of propane, butane and heavier hydrocarbons is effected in absorber 33 by absorption of these hydrocarbons in mineral seal oil in the conventional manner. The hydrocarbon rich-mineral seal oil is withdrawn from the lower portion of absorber 33 and is passed to a stripping column 36 via line 34. Light hydrocarbons, such as propane, butane, etc., are stripped from the mineral seal oil by lowering the pressure or heating in stripping column 36. Recovered hydrocarbons from stripping column 36 are passed via line 38 and condenser 39 to accumulator 41. Stripped mineral seal oil is recirculated to absorber 33 by means of line 42. Light gases such as hydrogen, methane, carbon monoxide, are removed from absorber 33 through line 43 and discarded or used as fuel, if desired. These gases may also be passed to a second and smaller reactor (not shown) for the conversion of the remaining hydrogen and carbon monoxide to hydrocarbons.

Liquid hydrocarbons from settler 31 and accumulator 41 are passed via lines 46, 47 and 48 to fractionator 49 wherein desired products are separated and recovered. Light gases are withdrawn from fractionator 49 through line 51. Hydrocarbons boiling between 25 and 200° C. are withdrawn through line 52 for processing into a finished gasoline, and heavier hydrocarbons boiling above about 200° C. are removed by line 53. A portion of the fraction separated which boils between 25 and 200° C. is recycled to reactor 16 through lines 54 and 17 to promote the yield of normally liquid hydrocarbons formed by the hydrogenation of the carbon monoxide. If desired, a portion or all of the heavier hydrocarbons boiling above 200° C. may be passed to cracking unit 57 where the heavier hydrocarbons are thermally or catalytically cracked, under appropriate conditions known in the art, to lighter hydrocarbons, usually olefinic hydrocarbons, boiling in a range between 25 and 200° C. From cracking unit 57, this light hydrocarbon fraction is then passed to reactor 16 through lines 58, 54 and 17 to promote the yield of normally liquid hydrocarbons. Both hydrocarbon fractions from line 52 and line 58 may be introduced simultaneously into reactor 16, or either of the fractions may be sufficient alone; thus, either one or both of the fractions may be introduced into reactor 16. A portion or all of the effluent from cracking unit 57 may be discharged from the system through line 59 for other uses or further treatment, if desired.

EXAMPLES

The following examples illustrate the utility and advantages of recycling a portion of the synthesis product to the reaction zone. Example I shows the synthesis of hydrocarbons from 100 litres of synthesis gas comprising hydrogen and carbon monoxide in the presence of a cobalt-thoria catalyst without recycling or introducing a hydrocarbon into the reaction zone as described in this invention.

EXAMPLE I.

CONDITIONS.

Feed Stock:	Molar ratio of $H_2:CO=2:1$ 100 litres of gas
Temperature	200° C.
Pressure	100 p.s.i.g.
Space Velocity	100

HYDROCARBON PRODUCT.

Components	Weight %
Hydrocarbons boiling below 25° C.	2
Hydrocarbons boiling between 25° and 200° C.	58
Liquid hydrocarbons boiling above 200° C.	34
Waxes	6
	100

Analysis of liquid fraction boiling below 200° C.

Total unsaturates, 50%

Yield: 6 cc. of hydrocarbons boiling between 25° and 200° C. per 100 litres of synthesis gas.

Total hydrocarbons above ethane in effluent = 65 wgt. %

EXAMPLE II.

Example II shows the results obtainable in the presence of a cobalt-thoria catalyst when an intermediate fraction boiling between 25 and 200° C. is separated from the hydrocarbon product and is recycled to the reaction zone under similar reaction conditions as in Example I.

CONDITIONS:

Feed Stock:	Molar ratio of $H_2:CO=2:1$ 100 litres of gas
Temperature	200° C.
Pressure	100 p.s.i.g.
Space Velocity	100
Recycle of 25—200° C. fraction	4 Volumes of recycle per 100 volumes of feed stock.

PRODUCT.

Components	Weight %
Hydrocarbons boiling below 25° C.	1
Hydrocarbons boiling between 25° and 200° C.	60
Hydrocarbons boiling above 200° C.	39
	100

Yield: 10 cc. of hydrocarbons boiling between 25 and 200° C. produced per 100 litres of synthesis gas.

It is evident, therefore, that the recycle of a hydrocarbon fraction increases the yield of normally liquid hydrocarbons as much as 66% or more.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the synthesis of hydrocarbons having more than one carbon atom in the molecule which comprises reacting hydrogen with carbon monoxide at a temperature such that hydrocarbons are produced and at a pressure of from 15 to 2000 p.s.i.g. in the presence of a catalyst comprising a metal from Group VIII of the periodic table and introducing into the reaction zone a hydrocarbon fraction boiling between 25° and 200° C. and comprising straight and/or branched chain saturated or unsaturated hydrocarbons, said hydrocarbon fraction being wholly in the vapour phase under the conditions of the reaction.

2. A process for the synthesis of normally liquid hydrocarbons from hydrogen and carbon monoxide which comprises reacting hydrogen and carbon monoxide, in the presence of a catalyst comprising a metal from Group VIII of the periodic table at a pressure of from 15 to 2000 p.s.i.g. and at a temperature at which normally liquid hydrocarbons are formed, withdrawing an effluent from the reaction zone, separating from the effluent a hydrocarbon fraction boiling between 25° and 200° C. and comprising straight and/or branched chain saturated or unsaturated hydrocarbons, and recycling at least a portion of said fraction to the reaction zone where it is present wholly in the vapour phase.

3. A modification of the process according to claim 2, in which the recycled fraction is obtained by subjecting to cracking conditions a fraction boiling above 200° C. separated from the withdrawn effluent.

4. A process according to either of claims 2 or 3, which comprises recycling between 5 and 7 parts by weight of separated hydrocarbons per 10 parts of total hydrocarbons product.

5. A process according to any one of the preceding claims, in which the fraction introduced into the reaction zone comprises a hydrocarbon having not less than 5 and not more than 12 carbon atoms per molecule.

6. A process according to any one of the preceding claims, in which the fraction introduced into said reaction zone is an unsaturated aliphatic hydrocarbon.

7. A process according to claim 6, in which the fraction is predominantly olefinic.

8. A process according to any one of the preceding claims, which comprises reacting hydrogen and carbon monoxide in the reaction zone in the presence of the synthesis catalyst containing iron or cobalt, at a pressure between 15 and 500 pounds per square inch gauge, maintaining the molar ratio of hydrogen to carbon monoxide between 3:2 and 1:1, and maintaining a space velocity between 100 and 150.

9. A process according to claim 8, which comprises reacting the hydrogen and carbon monoxide in the reaction zone in the presence of an iron synthesis catalyst at a temperature between 210 and 280° C.

10. A process according to claim 8, which comprises reacting the hydrogen and carbon monoxide in the reaction zone in the presence of a sintered iron synthesis catalyst at a temperature between 265 and 350° C.

11. A process according to claim 8, which comprises reacting the hydrogen and carbon monoxide in the reaction zone in the presence of a cobalt-thoria synthesis catalyst at a temperature between 180 and 250° C.

12. The processes for the synthesis of hydrocarbons substantially as set forth in Example II.

13. Hydrocarbons whenever prepared

by a process according to any one of the preceding claims.

Dated the 28th day of August, 1946.
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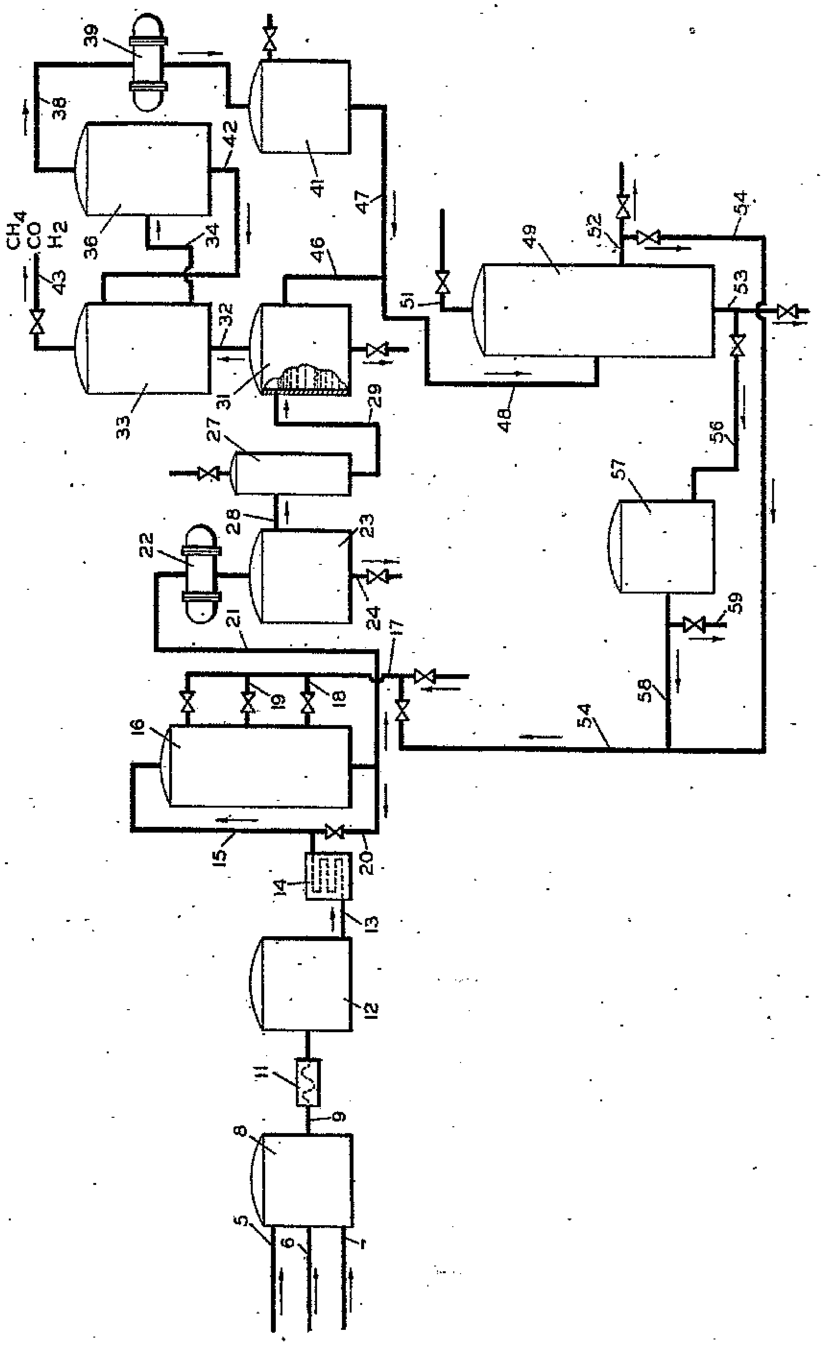

H.M.S.O.(Ty.P.)