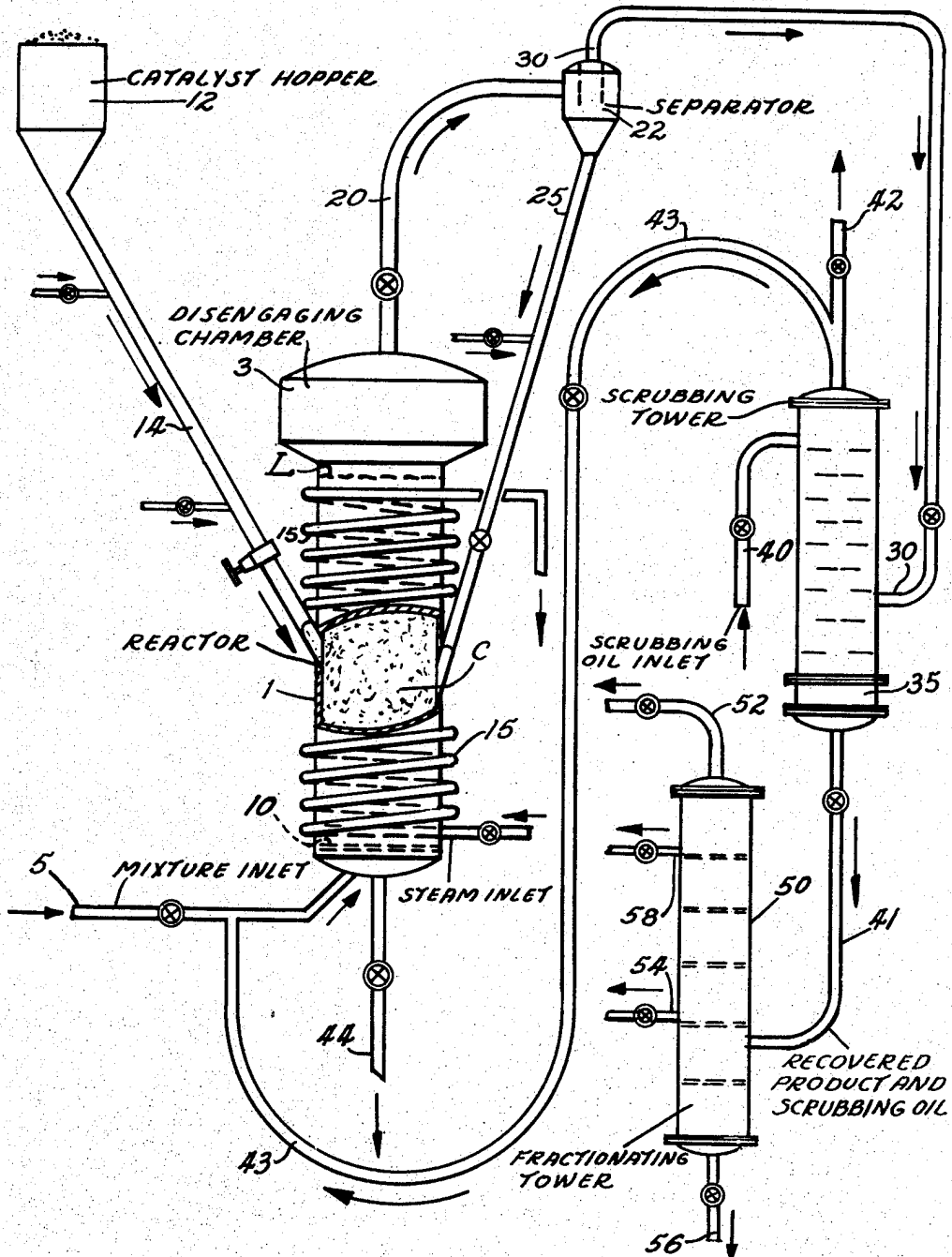


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SYNTHESIS OF HYDROCARBONS  
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## SYNTHESIS OF HYDROCARBONS

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The present invention relates to the synthesis of hydrocarbons from carbon oxides and hydrogen in the presence of a suitable catalyst. More particularly, the invention is concerned with the production of normally liquid hydrocarbons having specific highly desirable properties, by the catalytic conversion of carbon monoxide with hydrogen.

The synthesis of hydrocarbons and oxygenated compounds from carbon monoxide and hydrogen is already known. It has also been suggested, prior to the present invention, to select the reaction conditions of temperature, pressure, contact time, feed gas ratio, etc. as well as the nature of the catalyst as a function of the specific type of product desired. For example, cobalt catalysts have been used at relatively low temperatures of about 350°-450° F. and relatively low pressures of about 1-10 atmospheres abs. to form predominantly saturated paraffinic liquid and solid hydrocarbons from which highly valuable Diesel fuels and lubricating oils, but only low octane number motor fuels may be obtained. Iron catalysts in combination with higher temperatures of 450°-650° F. and higher pressures of about 3-25 atmospheres abs. have been employed where a predominantly unsaturated product is desired from which valuable motor fuels having relatively high octane ratings may be recovered. Still higher pressures of up to 100 atmospheres abs. and above favor the formation of high yields of oxygenated compounds.

While it has been thus possible, prior to the present invention, to synthesize from CO and H<sub>2</sub> a straight run gasoline having a research octane number of up to about 75, particularly when using iron catalysts, attempts of raising this octane number to or above 80 by mere variation of the synthesis conditions while maintaining the yields at economical levels have not been practically successful. However, straight run research octane numbers of at least 80 are essential for an economical production of motor fuels having research octane numbers of 95 and above as they are required by modern automotive and aviation engines. The present invention is concerned with a process which permits the production from CO and H<sub>2</sub>, of economical yields of a straight run gasoline having research octane numbers

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substantially higher than those obtainable by prior art processes.

It is, therefore, the principal object of the present invention to provide an improved process for the conversion of CO with H<sub>2</sub> to form normally liquid hydrocarbons.

A more specific object of the present invention is to provide an improved hydrocarbon synthesis process by which high octane number gasoline may be produced.

Other and more specific objects and advantages of the invention will appear hereinafter.

I have found that these objects may be accomplished by contacting mixtures of CO and H<sub>2</sub> in synthesis proportions with a dense, turbulent, fluidized mass of finely divided iron catalyst at temperatures in excess of 700° F. and, preferably, within the range of about 700°-750° F. More particularly, my investigations have demonstrated that high temperatures of the order indicated are characteristically conducive to the formation of a gasoline containing high percentages of saturated and unsaturated branched chain hydrocarbons as well as appreciable quantities of aromatics and naphthenes, which are all high octane number constituents and which are not found to any appreciable extent in synthetic gasolines produced at the conventional lower temperatures. In the further development of this discovery I have found that the application of the so-called fluid catalyst technique permits high temperature operation of the type specified without excessive losses in the form of hydrocarbon gases, as well as a correlation of the other reaction conditions such as pressure, feed gas ratio, contact time, gas recycle ratio, etc. affording excellent and economical yields of the improved octane number gasoline.

I am aware of the fact that high synthesis temperatures of, say, about 700° or 750° F. have been suggested before in the literature and numerous patent specifications. However, temperatures in this high range have not been employed in practice and their effect on product characteristics has not been fully explored or known heretofore. Probably the most important single factor responsible for this limitation in the development of the hydrocarbon synthesis must be found in the fact that practically all experimental and development work carried out in the past em-

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ployed fixed bed operation and has demonstrated temperatures above about 650°-700° F. to be the cause of excessive losses of synthesis gas in the form of methane without my compensation in the form of appreciably improved product qualities. The experience gained in the previous fixed bed work has created an extremely strong prejudice against high temperature operation, which has been carried over into the more recent work on fluid operation with the result that the art has refrained from the use of temperatures above 700° F. in fluid operation as well. I have found, however, that the detrimental effects of high temperature operation are bound to the fixed bed technique which involves local overheating of the catalyst causing loss of catalyst selectivity while, as a result of the excellent heat transfer efficiency and greatly improved temperature control of the fluid catalyst technique, these detrimental effects are eliminated and, in addition, the above mentioned improvements in product quality may be obtained.

While the combination of the fluid catalyst technique with high temperature operation within the range indicated affords, quite generally, a motor fuel product of improved quality, best results with respect to both quality and quantity of the gasoline yield are obtained when the other reaction conditions are carefully correlated to the temperature and specific catalyst used. Thus, I have found that yields of more than 200 c. c. C<sub>3</sub>+hydrocarbons containing about 60 to 75% of gasoline having a boiling range of about 100°-400° F. and a research octane number of at least 80 may be obtained per cu. m. of CO+H<sub>2</sub> consumed when a fluidized iron catalyst prepared from pyrites or sintered pure iron and promoted with 0.1 to 1.5%, preferably 0.6-0.9% of potassium (the percentage expressed as % of K<sub>2</sub>O on Fe<sub>2</sub>O<sub>3</sub>), in the form of its compounds such as the carbonate, is used at a temperature from above 700° to about 850° F., preferably between about 700°-750° F.; a pressure of 150-1500 lbs. per sq. in. gage, preferably 200-400 lbs. per sq. in. gage; a synthesis gas feed rate of about 20-50 normal cu. ft. of CO and H<sub>2</sub> per lb. of catalyst per hour; an "effective" H<sub>2</sub>:CO ratio<sup>1</sup> in the fresh feed gas of about 0.7-1.9; and a recycle of exit gases to the reactor in the amount of 0-3, preferably 0-1.0 volumes per volume of fresh feed gas.

At these conditions, total conversion of CO and H<sub>2</sub> and selectivity to liquid high octane products are at a maximum mainly due to the high temperature while losses in the form of methane are kept below 10% as a result of perfect temperature control. The preferred low promoter concentration effectively reduces the production of oxygenated compounds although where high yields of these latter are desired, catalysts using higher amounts of promoter may be used.

The process of the present invention may be carried out in any conventional equipment adapted to fluid catalyst operation. A system suitable for this purpose is shown semi-diagrammatically in the accompanying drawing which will now be described in order to illustrate, in greater detail, the operation of the invention. It should be understood, however, that the invention is not limited to any of the specific features shown in the drawing which permits of numerous modifications obvious to those skilled in the art without deviating from the spirit of the invention.

Referring now in detail to the drawing, 1 rep-

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resents a reactor which is preferably in the form of a vertical cylinder having an upper expanded section 3. A synthesis gas feed mixture of hydrogen and carbon monoxide in the ratio of about 1.2 to 1.9 mols of H<sub>2</sub> to 1 mol of CO is introduced into the reactor through line 5 and flows upwardly through a perforated member 10 such as a distributing grid or screen which is inserted to assure proper distribution of the gases.

Within reactor 1 a mass of iron catalyst C of the type described above is maintained in the form of a powder having a particle size of about 200 to 400 mesh, preferably in such size distribution that 90-95% has a particle size of 300 mesh. When starting up the process, this catalyst may be supplied to reactor 1 from catalyst hopper 12 through pipe 14.

The linear velocity of the gases within reactor 1 is kept within the approximate range of 0.3 to 5 ft. per second, preferably within the range of 0.5 to 1.5 ft. per second, for the catalyst sizes indicated above. If, however, larger catalyst particles, say, up to ¼" in diameter are used, the linear gas velocity may be as high as 5 to 10 ft. per second.

At the conditions of particle size and gas flow indicated, the catalyst takes on the form of a dense, turbulent, ebullient mass resembling a boiling liquid having a well defined upper level L and an apparent density of about 30 to 150 lbs. per cu. ft. depending on the fluidization conditions. The fluidized mass extends from the grid plate 10 to level L and the catalyst particles move in all conceivable directions through the fluidized mass. The amount of synthesis gas supplied through line 5 is so controlled that about 20-50 normal cu. ft. of fresh synthesis gas enter reactor 1 per lb. of iron catalyst per hour and the pressure within reactor 1 is preferably adjusted to about 200-400 lbs. per sq. in.

When entering enlarged section 3 of reactor 1, the gas velocity is sufficiently decreased so that the gases will no longer support any substantial quantity of catalyst and most of the catalyst particles entrained in the gas drop back into the fluidized mass below level L.

The reaction temperature of the highly exothermic synthesis reaction is controlled with the aid of a cooling jacket or cooling coil 15 which surrounds the outside wall of the reactor. Any heat exchange medium, such as steam, mixtures of diphenyl and diphenyl oxide, or the like, may be passed through jacket or coil 15 in the manner indicated in order to establish a uniform temperature between the approximate limits of 700°-750° F. within the fluidized catalyst mass C. As a result of the ideal heat distribution and heat transfer characteristics of the fluidized catalyst mass, the temperature may be kept uniform over the entire length and diameter of the catalyst mass within a few degrees F. by cooling means of the type illustrated.

Volatile reaction products, substantially depleted of entrained catalyst, are withdrawn through line 20 and, preferably, passed through a gas solids separator 22 which may be a cyclone, an electrical precipitator, or any other type of conventional separator. The last traces of entrained catalyst fines are separated in separator 22 and may be returned to reactor 1 through line 25.

Product vapors and gases, free of entrained solids, are withdrawn overhead from separator 22 through line 30 and may be discharged into a conventional scrubber 35 where normally liquid

<sup>1</sup>The "effective" ratio is (H<sub>2</sub>-CO<sub>2</sub>) : (CO+CO<sub>2</sub>).

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hydrocarbons are recovered by scrubbing with oil or the like supplied through line 40, in a manner known per se. Tail gas is withdrawn overhead from scrubber 35 and may either be vented through line 42 or recycled to gas feed line 5 through line 43, preferably in a ratio not greater than .5 volume of recycle gas per volume of fresh feed gas.

The scrubbing oil and recovered hydrocarbons are removed from scrubbing tower 35 through line 41 and passed to a fractionating column 50. Normally gaseous hydrocarbons are taken overhead from column 50 through line 52 while fractions heavier than gasoline may be removed through lines 54 and 56. A fraction boiling within the motor fuel range and containing high percentages of branched chain hydrocarbons, aromatics and naphthenes is recovered through line 58. The latter fraction which normally has a research octane number of about 80-85 may be further refined by a treatment with silica alumina cracking catalyst in a manner known per se, whereby its octane number may be raised to values above 95.

When a new charge of catalyst is desired, the spent catalyst may be withdrawn through line 44 and new catalyst supplied through line 14.

As pointed out before, the system shown in the drawing permits of many modifications. For example, instead of using a cooling jacket or coil as illustrated, cooling means may be imbedded in the fluidized catalyst mass or the catalyst may be continuously withdrawn through line 44, passed through a cooling zone and returned to reactor 1 in a manner known per se. The product recovery system illustrated may be supplemented or, in part, substituted by solid adsorbent equipment such as towers filled with activated char coal, silica gel, or the like. Other modifications may appear to those skilled in the art.

The invention will be further illustrated by the following specific examples.

#### Example I

A catalyst obtained by reducing and sintering in H<sub>2</sub> at 1000°-1200° F. a precipitated iron oxide containing 1% KF promoter was used in conventional fixed bed operation at the conditions and with the results given below:

Run No.	I	II
Temperature, °F.	600	650
Pressure, p. s. i. g.	150	150
Feed, v./v./hr.	200	200
Ratio, H <sub>2</sub> /CO	1.7	1.8
Per Cent CO Conv.	98	98
Per Cent CO+H <sub>2</sub> Conv.	75	78
Yields:		
C <sub>2</sub> +, cc./M. <sup>3</sup> H <sub>2</sub> +CO Cons.	222	200
C <sub>4</sub> +, cc./M. <sup>3</sup> H <sub>2</sub> +CO Cons.	155	141
Hydrocarbon Distribution Per Cent CO to Hydrocarbons in—		
C <sub>1</sub>	11	17
C <sub>2</sub> Compounds	11	12
C <sub>3</sub> Compounds	18	16
C <sub>4</sub> + Compounds	60	55

A comparison of the data of runs I and II, obtained at substantially identical reaction conditions except for the temperatures used, shows a drop in liquid yield of about 10% and an increase in gas formation of about 50% for a rise in temperature of 50° F. No applicable change was observed in the research octane number which normally lines at about 75 for synthetic gasolines obtained at the conditions specified. Operation at temperature higher than 650° F. greatly increases the trend indicated by the above data.

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#### Example II

Two fluid catalyst runs were carried out using an iron catalyst obtained by reducing with hydrogen at 700° F. an oxidic material of the following composition:

	Parts by weight
Fe	67.1
O <sub>2</sub> combined with Fe	26.1
Al <sub>2</sub> O <sub>3</sub>	2.57
SiO <sub>2</sub>	1.37
MnO	.85
K <sub>2</sub> O	.90
MgO	.11
CuO	.10
NiO	.05

The catalyst particle size was as follows:

	Percent
0-20 microns	20
20-40 microns	17
40-60 microns	27
60-80 microns	36

The reaction conditions and yields of these two runs were as given below:

Run No.	III	IV
Temperature, °F.	655	705
Pressure, p. s. i. g.	397	386
Recycle	1.9	3.0
Feed, v./v./hr.	33	33
Ratio, H <sub>2</sub> /CO, effective	1.3	1.3
Velocity, ft./sec.	.89	.90
Per Cent CO Conv.	96.5	97.1
Per Cent CO+H <sub>2</sub> Conv.	92.5	95.2
Yields:		
C <sub>2</sub> +, cc./M. <sup>3</sup> H <sub>2</sub> +CO Cons.	229	233
C <sub>4</sub> +, cc./M. <sup>3</sup> H <sub>2</sub> +CO Cons.	179	179
Hydrocarbon Distribution, Per Cent CO to Hydrocarbons in—		
C <sub>1</sub>	6.1	7.4
C <sub>2</sub> Compounds	8.4	8.1
C <sub>3</sub> Compounds	11.1	10.5
C <sub>4</sub> + Compounds	65.4	68.5
Oxygenated Compounds	9.0	5.5
Liquid Distribution of C <sub>4</sub> +		
C <sub>4</sub> -400° F.	25	20
400° F. +	63	64
Research O. N. of C <sub>4</sub> -400° Gasoline	12	16
	75.7	84.0

The data of runs III and IV shows that when the fluid solids technique is applied at the conditions of the present invention (run IV) an increase in temperature of about 50° F. beyond the temperature range causing appreciable cracking in fixed bed operation (run II) results in a considerable increase of the research octane number without any reduction in liquid yield or any substantial increase in gas formation.

While the foregoing description and exemplary operations have served to illustrate specific applications and results of my invention, other modifications obvious to those skilled in the art are within the scope of my invention. Only such limitations should be imposed on the invention as are indicated in the appended claims.

I claim:

1. An improved process for producing valuable conversion products from CO and H<sub>2</sub> by a catalytic synthesis reaction which comprises contacting a synthesis feed gas mixture containing H<sub>2</sub> and CO in the approximate effective ratio of 1.3 at a temperature of approximately 705° F. with a dense, turbulent, fluidized mass of a finely divided iron catalyst promoted with about 1.1% by weight of potassium calculated on iron, while maintaining a pressure of about 386 lbs. per sq. in. gage, a fresh synthesis feed gas rate of about 33 normal cu. ft. of gas per lb. of catalyst per hour, a recycle to fresh feed gas ratio of about

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3, a CO conversion of about 97% and a CO+H<sub>2</sub> conversion of about 95.2%, withdrawing volatile products from said catalyst mass and recovering from said withdrawn products a hydrocarbon fraction of the motor fuel boiling range rich in branched chain paraffinic and olefinic hydrocarbons, aromatics and naphthenes, said fraction having a research octane number of about 84.

2. The process of claim 1 wherein said iron catalyst essentially comprises sintered pure iron.

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