

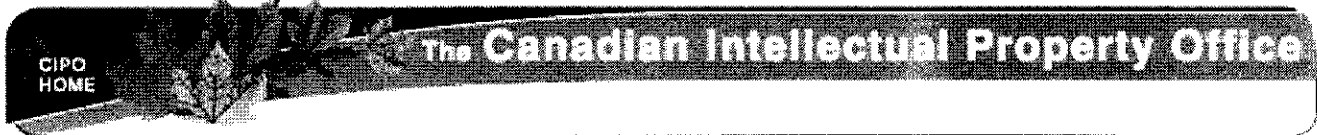


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(54) SYNTHESIS OF LIQUID HYDROCARBONS FROM HYDROGEN AND CARBON MONOXIDE

(54) SYNTHÈSE D'HYDROCARBURES LIQUIDES D'HYDROGÈNE ET D'OXYDE DE CARBONE

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The present invention relates to the synthesis of hydrocarbons from gaseous feed stocks containing hydrogen and carbon monoxide. More particularly, it pertains to the provision of a combination of operating conditions whereby hydrocarbon synthesis is effected in a manner such that a maximum quantity of useful products is obtained at high total feed carbon monoxide conversions.

10 It is generally known that liquid hydrocarbons as well as various oxygenated organic chemicals can be synthesized by reducing carbon monoxide with hydrogen in the presence of a fluidized iron catalyst at temperatures in the range of 550 to 675^oF. and at pressures in the range of 150 to 350 p.s.i. (pounds per square inch). Prior workers in this field were confronted with many difficult problems in their effort to conduct this reaction in a manner such that maximum quantities of desired products would be produced. In attempting to accomplish this result, various combinations and ranges of conditions have been taught; however, the wide range of operating variables described in
20 the prior art covers many conditions under which it is extremely uneconomical or undesirable to operate. In no single instance of which we are aware has any worker in this field revealed a specific combination of operating variables whereby maximum yields of desired products can be obtained.

Accordingly, it is an object of our invention to provide a hydrocarbon synthesis process capable of producing a maximum amount of desired products while obtaining only a relatively insignificant proportion of undesirable end products.

Specifically, it is an object of our invention to provide a combination of operating conditions, the utilization of which results in the procurement of optimum yields of desirable end products together with only a minor amount of unusable materials.

Previously, it was thought that the composition of the reactor feed was of prime importance with respect to the nature and distribution of the products produced as well as the performance of the process itself, i.e., proper fluidization of the catalyst, etc. We have found, however, that when carrying out the synthesis within the particular ranges of operating conditions herein set forth, total feeds containing as much as 18 to 20 per cent carbon monoxide or even higher concentrations may be utilized without the deleterious results previously thought to be caused by such "excessive" concentrations of carbon monoxide.

Fundamentally, our invention involves the discovery that at high total feed carbon monoxide conversions, i.e., of the order of about 90 to 95 per cent, and preferably about 92 per cent, the selectivity of carbon monoxide conversion to useful products such as, for example, hydrocarbons containing 3 or more carbon atoms, hereinafter referred to as C_{3+} , reaches a maximum while the production of undesirable end products is held to a minimum value. Although it has been our observation that high conversions of carbon monoxide in the total reactor feed should be maintained to achieve high selectivities to useful products, this result cannot be secured without simultaneously utilizing specific ranges of temperature, pressures, recycle ratios, space velocities, and hydrogen

partial pressures. Thus, to procure the desired selectivity of total feed carbon monoxide to useful products the following operating conditions should be employed: temperatures of from about 600 to about 670°F., preferably about 650°F.; pressures of from about 325 to about 425 p.s.i. (pounds per square inch), preferably about 375 p.s.i. (pounds per square inch); a ratio of hydrogen to carbon monoxide in the fresh feed of from about 1.5 to about 2.0, preferably from about 1.7 to about 1.8; recycle of tail gases in a ratio of from
10 about 1.2 to about 1.7 volumes per volume of fresh feed, preferably a ratio of 1.5:1 and space velocities (fresh feed basis - F.F.) in the range of 3.0 to 4.0 SCFH CO/pound of iron catalyst. Failure to employ the aforesaid ranges of operating conditions results in a lower selectivity to useful products, i.e., the C₃₊ fraction. With recycle ratios less than 1.2:1 the selectivity to useful products drops off sharply even though the other conditions specified above remain well within the recommended limits. Although recycle ratios in excess of 1.7 may be employed, the beneficial
20 effect obtained by so doing is insignificant in comparison to the expenditure required for the auxiliary equipment necessary at these high recycle ratios. We have further found that space velocities below those recommended require a substantial increase in reactor size with little or no gain in conversion, while space velocities in excess of those herein specified reduce conversions and selectivity to the C₃₊ fraction, result in high reactant losses, and an increase in carbon dioxide production. We have also observed that

pressures of from 325 to 425 p.s.i. (pounds per square inch) favor maximum conversion of carbon monoxide to the desired C_{3+} fraction while the production of carbon dioxide and C_1 and C_2 hydrocarbons is held to a minimum. Thus, when employing the above-stated pressure range and the other operating conditions taught herein, we have found that as much as 78 per cent of the total feed carbon monoxide converted consists of the desired C_3 and heavier products fraction. Production of carbon dioxide and C_1 and C_2 hydrocarbons within the aforesaid preferred pressure range is found to be as low as 21 per cent of the total carbon monoxide converted while at pressures above or below the above-mentioned range, e.g., at pressures of about 450 p.s.i. (pounds per square inch), the concentration of carbon dioxide and C_1 and C_2 hydrocarbons increases to 26 per cent and at pressures below 325 p.s.i. (pounds per square inch), conversion of total feed carbon monoxide to C_3 and heavier products drops off rapidly while carbon dioxide production increases. Temperatures of from about 600 to 670°F. may be employed, 650°F. being generally preferred from the standpoint of good conversion and long catalyst life. At temperatures below 600°F. the reaction rate diminishes and fluidization problems occur while at temperatures above 670°F., the activity of the catalyst decreases rapidly. Thus, for example, in a run in which a temperature of 680°F. was employed, total feed carbon monoxide conversion declined from a high of 87 per cent to 70 per cent, while in a second run in which all conditions were identical with those employed in the first instance, with the exception of temperature which was 650°F., total

feed carbon monoxide conversion declined from 87 per cent only to 77 per cent over the same time interval.

It will be observed that the operating conditions herein disclosed and regarded by us to be critical in so far as concerns optimum selectivities of total feed carbon monoxide to the C_{3+} fraction apply in general to iron-type hydrocarbon synthesis catalysts. However, we have noted these conditions to be particularly suited to the procurement of high selectivities to the desired C_3 and heavier
10 hydrocarbon fraction when employing the catalyst commonly designated as mill scale which is described and claimed in U.S. Patent No. 2,485,945 granted October 29, 1949 to S.W. Walker. This catalyst is prepared from the oxide scale or layer obtained by rolling iron or various alloys thereof at elevated temperatures, for example, in the range of 1000 to 1300°C. Microscopic examination of the scale or oxide layer thus obtained when ground to a fineness of the order of 325 mesh indicates that it still retains its characteristic plate-like structure.

20 Our invention will be more clearly understood from the accompanying graphs, the curves of which are based upon actual synthesis runs employing mill scale catalyst and further demonstrate the important and close relationship existing between various ranges of the operating conditions herein specified and the optimum selectivity of C_3 and heavier hydrocarbons at high total feed carbon monoxide conversions.

In the accompanying drawings:

Figure 1 is a graphic representation of the effect of recycle ratio and space velocity on total feed carbon
30 monoxide conversion.

Figs. 2 and 3 are graphs illustrating the effect of recycle ratio on selectivity to carbon dioxide and the C_{3+} fraction, respectively.

Fig. 4 is a graph demonstrating the effect of temperature on total feed carbon monoxide conversion.

The mill scale catalyst employed in the runs on which the above-mentioned graphs are based was promoted with from about 0.5 to 0.7 per cent K_2O , based on the weight of the iron. Other alkaline promoters may
 10 be employed although potassium compounds are generally preferred. In all cases the mill scale was ground to a screen size of about 100 mesh and promoted with potassium carbonate in the usual fashion. The promoted base material was then reduced with hydrogen at $700^{\circ}F.$ and at 250 p.s.i. (pounds per square inch) until evolution of water could no longer be detected after which the catalyst was subjected to an activation period of twenty hours under the following conditions:

20	Fresh feed $H_2:CO$ ratio	1.85-1.9
	Pressure, pounds per square inch	400
	Recycle of fresh feed ratio	1.8
	Temperature	$650^{\circ}F.$
	Space velocity, SCFH of CO(F.F.) per pound of iron catalyst	4.0-6.0

These conditions are essentially those of synthesis except that the recycle ratio is higher than that normally employed. Linear velocity is not critical, fluidization being maintained at velocities as low as 0.25 foot per sec.; however, heat transfer is improved at the higher velocities. Some
 30 catalyst carryover depending, of course, on catalyst mesh size is experienced at 0.75 foot per sec. but any velocity may be used which is compatible with adequate fluidization

and reasonable catalyst recovery by a cyclone or equivalent system.

In the runs on which the curves appearing in Fig. 1 are based, the following conditions were established:

Fresh feed H ₂ :CO ratio	1.85
Pressure, pounds per square inch	400
Recycle to fresh feed ratio	1 to 2
Space velocity	2.5 to 11.1

From the curves in Fig. 1, it will be seen that the total
 10 feed conversion is lower at the higher recycle ratio. Fresh
 feed conversion, however, is slightly higher. A decrease in
 space velocity markedly increases conversion down to space
 velocities of 4.0 SCFH CO/pound iron. Beyond this point
 conversion does not increase significantly with a decrease
 in space velocity. Lowering the space velocity below 3.5
 to 3.0 requires an increase in reactor size with very little
 gain in conversion while space velocities higher than 4.0
 reduce conversion and selectivity to C₃₊ and result also in
 production of increased quantities of carbon dioxide and
 20 in less of reactants.

In Figs. 2 and 3 selectivities to carbon dioxide
 and to the C₃₊ fraction, respectively, are plotted against
 conversion at recycle ratios of 1, 1.5, and 2. The data
 appearing in these graphs were obtained under the same oper-
 ating conditions as those in Fig. 1. Fig. 2 illustrates the
 extremely important but hitherto unrecognized fact that
 carbon dioxide production increased with decreasing total
 feed carbon monoxide conversion and decreasing recycle
 ratios. Fig. 3 demonstrates the per cent carbon monoxide
 30 conversion to C₃₊ hydrocarbons and chemicals at different

total feed carbon monoxide conversions and at recycle ratios ranging from 1 to 2. The information shown by Fig. 3 indicates that recycle ratios of from about 1.2 to 1.7 are preferable to achieve selectivities of 67 to 73 per cent of converted carbon monoxide to useful products. Although it is indicated that higher recycle ratios might be desirable, we have found that their use is unwarranted from the standpoint of efficiency and economy. The utilization of recycle ratios below 1.2 results in substantially decreased C_{3+} selectivity owing to increased carbon dioxide production, as indicated in Fig. 2, and loss of reactants. From the slopes of these curves it can be seen that selectivity is sensitive to changes in conversion. Also, the position of the curves indicates importance of recycle ratio. This effect of recycle ratio on carbon dioxide formation and the production of the desired C_{3+} hydrocarbons and chemicals fraction has previously been unrecognized. However, we have found that the above-mentioned recycle range, when employed in combination with the other operating conditions herein described, is responsible for the procurement of high conversions of total feed carbon monoxide and a correspondingly high selectivity of such converted carbon monoxide to the desired C_{3+} fraction.

The curve shown in Fig. 4 is based on three separate synthesis runs carried out under identical operating conditions with the exception of temperature. The effect of temperature on total feed carbon monoxide conversion is clearly shown. The range of 600 to 670^oF. defines the temperature limits which we have found to be most satisfactory from the standpoint

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of production of maximum useful products. The adverse results obtained when operating above and below the temperature range herein specified have been pointed out previously.

10 From the foregoing description as well as the graphs presented, it will be seen that an extremely close relationship exists between the combination of relatively narrow operating conditions taught herein and the maximum conversion of carbon monoxide to useful products in the synthesis of hydrocarbons by the reduction of carbon monoxide with hydrogen in the presence of a fluidized catalyst. Moreover, it has been demonstrated that a departure from our recommended range of any single set of operating conditions, i.e., temperature, recycle ratio, space velocity, etc., causes a substantial reduction in the ultimate yield of useful products. In addition, we have shown for the first time the important relationship between recycle ratio and space velocity and the effect of these conditions on total feed carbon
20 monoxide conversion and on selectivity to useful products.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for obtaining maximum yields of C_{3+} hydrocarbons and chemicals by the reduction of carbon monoxide with hydrogen in a reaction zone and in the presence of a fluidized iron catalyst, which comprise contacting said catalyst with a fresh feed gas containing major proportions of hydrogen and carbon monoxide in a ratio ranging from 1.5:1 to 2.0:1 at a temperature of from about 600 to 670°F., a pressure of from 325 to 425 p.s.i. (pounds per square inch) and space velocities of from 3.0 to about 4.0 SCFH CO/pound iron to produce gaseous and normally liquid hydrocarbons and oxygenated organic compounds, withdrawing from said reaction zone effluent comprising gaseous and normally liquid hydrocarbons, carbon dioxide, carbon monoxide, and hydrogen, separating the normally gaseous constituents of said effluent from the normally liquid components thereof, and recycling a sufficient quantity of said normally gaseous constituents to said reaction zone to maintain in the reactor total feed from 1.2 to 1.7 volumes of recycle gas per volume of fresh feed.

2. A process according to claim 1, in which the catalyst employed is derived from mill scale.

3. A process according to claim 1, in which the following operating conditions are established:

Mill scale catalyst promoted with an alkali metal compound

Temperature about 650°F.

Pressure about 375 pounds per square inch

Space velocity from 3.0 to about 4.0 SCFH CO/pound iron

$H_2:CO$ ratio in fresh feed 1.7 to 1.8

Recycle ratio about 1.5

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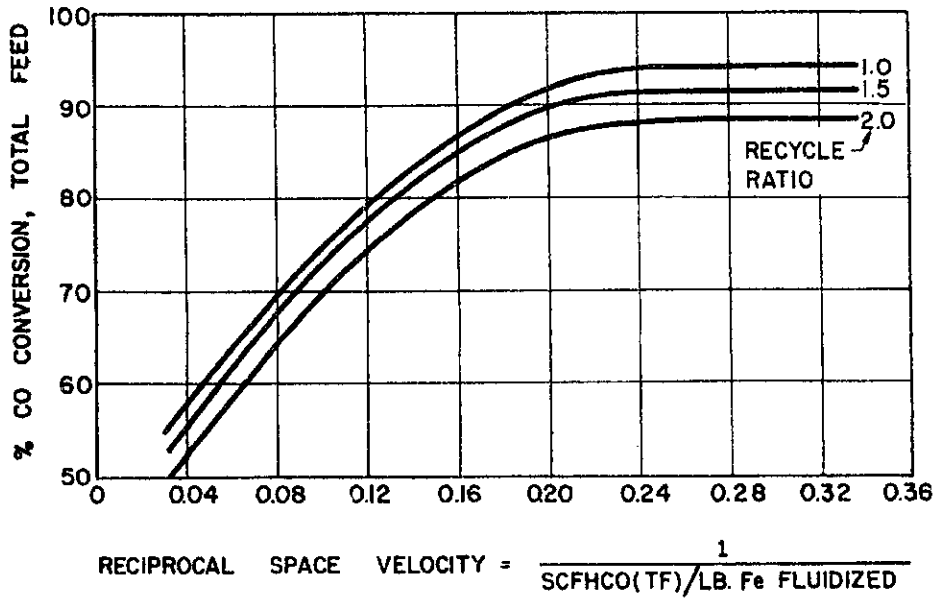


FIG. 1

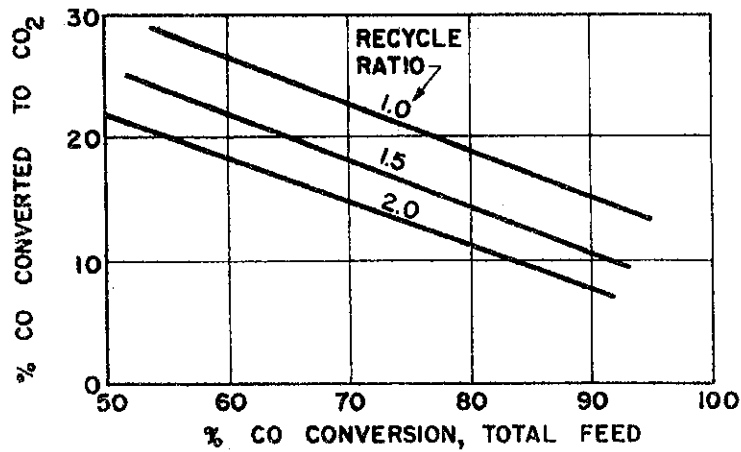


FIG. 2

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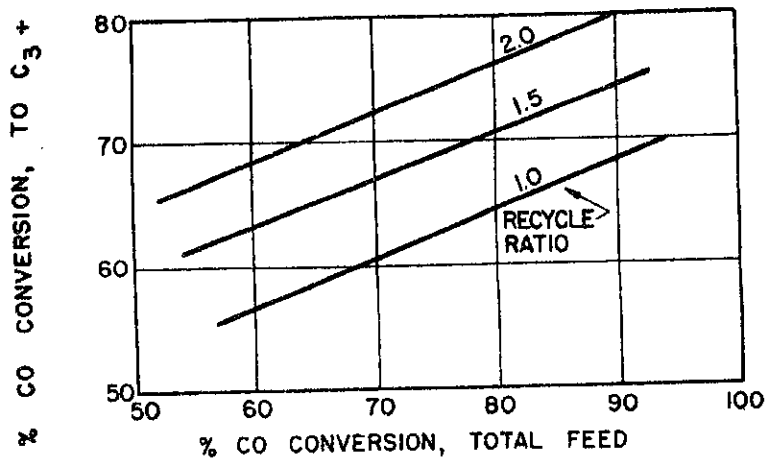


FIG. 3

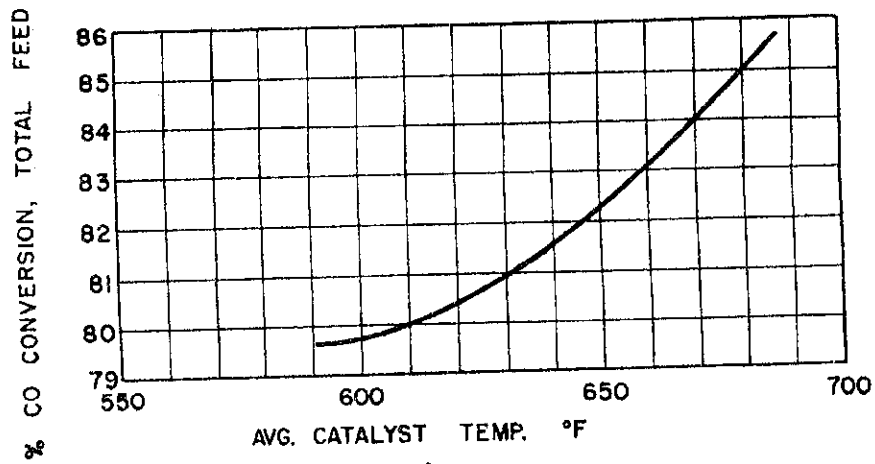


FIG. 4

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