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WARTIME RESEARCH ON SYNTHETIC FUELS

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KOHLNFORSCHUNG

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June 1945

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SUMMARY

Wartime research by the Kaiser Wilhelm Institut fur Kohlenforschung on the Fischer-Tropsch synthesis has been primarily directed along the line of iso-paraffin synthesis. Good yields of iso-paraffins have been obtained using the normal synthesis gas at three hundred (300) atmosphere pressure and four hundred twenty (420) to four hundred fifty (450) degrees centigrade over an alumina-thoria catalyst. Zinc oxide-alumina has also been used successfully. About one hundred twenty (120) to one hundred thirty (130) grams per cubic meter of synthesis gas have been obtained as liquid products of over ninety (90) percent iso-paraffins.

Synthesis of eromatics has been studied, using thirty (30) atmosphere pressure and five hundred (500) degrees centigrade. However, very poor yields and napthene side reactions do not make this process look promising. Further work was abandoned by KWI for the duration of the war.

Fischer-Tropsch synthesis using iron catalysts was studied, but inferior operations resulting from this catalyst made it only desirable as a wartime substitute for scarce chromium.

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1. DETAILS OF RESEARCH

(a) Iso-Paraffin Synthesis

(1) Operating conditions for the synthesis of iso paraffin have been found to lie in the range of three hundred (300) atmospheres pressure and four hundred twenty (420) to four hundred fifty (450) degrees centigrade. For pressure under three undred (300) atmospheres the yield falls off rather sharply, although a very slow reaction will take place at thirty (30) atmospheres or over. Higher pressures than three hundred (300) atmospheres give increasingly greater percentages of oxygenated products, until at one thousand (1000) atmospheres the principal product is dimethyl ether. Similarly, lower operating temperatures give slower reaction rates, more unsaturated compounds, a very high percentage of alcohols, and less carbon formation on the catalyst. For temperatures slightly greater than four hundred fifty (450) degrees centigrade, the products become principally napthenic, and carbon deposition becomes excescive. Instantaneous reaction rates, however, are increased.

(2) It has been found that the best synthesis gas has a CO/H_2 ration of 1.2 volumes of CO to one (1) of H_2. Increasing the hydrogen increases methane formation; decreasing the hydrogen lowers the overall yield.

(3) The best catalyst found for this synthesis has been an aluminathoria co-precipitated one, although ZnO-$A_1 2_O 3$ appears to be nearly as good and much cheaper. Using either of these materials it was found necessary to burn off the carbon deposits about every two weeks of steady operation. This was accomplished with air at the temperature of the synthesis (450) degrees centigrade. Catalysts so treated have been used continuously for over six (6) months without appreciable decline in activity. Their heat sensitivity is also quite good, as they have been held for prolonged periods at eight hundred (800) degrees centigrade without damage.

1. **DETAILS OF RESEARCH** (A) (cont'd).

(4) Heat evolution during synthesis is approximately the same as with the normal synthesis, i.e. one-fifth (1/5) of the heat of combustion of the products. Since it is possible to work in a twenty (20) to thirty (30) degree centigrade temperature range, this lessens the problem of very close temperature control normally encountered in this process. Another advantage is found in the fact that sulphur does not seem to be nearly as deleterious as in former syntheses, although the upper allowable limit has not yet been determined.

(5) Gas velocities have been fairly accurately studied, and it was determined that twenty (20) cubic centimeters of a two (2) to four (4) millimeter catalyst were necessary for each ten (10) liters of synthesis gas per hour. Any increase above this velocity gave sharp decreases in yield and also tended to form increasing amounts of alcohols.

(6) Product yields are as follows from a $ZnO-Al_2O_3$ catalyst using a CO/H_2 ratio of 1, at three hundred (300) atmospheres and four hundred fifty (450) degrees centigrade:

Total yield of C_3 and higher	120 - 130 gm./m^3
C_3	20 gm./m^3
C_4 (90% isobutane)	50 - 80 gm./m^3
C_5 and higher (over 97% iso)	30 - 60 gm./m^3

(7) A comparison of the two (2) catalysts shows that for a thoria-alumina catalyst (1:4 by weight) the best yields of all are obtained. Higher gas velocities can be used, and there is little tendency to form alcohols. However, there is a greater tendency to form carbon on the catalyst, meaning shorter burn-off times. Experiments have varied the ratio of the two materials in the catalyst from twenty (20) to forty (40) percent Al_2O_3, with very little change in overall yields. However, increased alumina does increase methane formation somewhat. The addition of one-half (½) to one (1) percent K_2CO_3 to the catalyst will give a slight increase in yield.

1. DETAILS OF RESEARCH (A) (cont'd).

(8) On the other hand the AnO-Al_2O_3 catalyst (1:1 by weight) is believed to carry more promise as a commercial catalyst because of its cheapness. It does give slightly less yield than the thoria type, and produces about ten (10) percent alcohols. There is less tendency to form carbon deposits on the catalyst. The same tendency holds true as with thoria catalysts, i.e., higher alumina content promotes methane formation. However, experiments have been made over a range of Al_2O_3 content from 2:1 to 1:2 without much change in results. Additions of K_2CO_3 do not appear to give any advantage.

(9) The thoria type catalyst was prepared by using two (2) liters of thorium and aluminum nitrates at their boiling point and in the right proportion to give a 1:4 weight ratio of thoria to alumina. This was added one (1) liter of a boiling Na_2CO_3 solution of proper strength to give one hundred (100) grams of dry co-ppt., in stoiciometric amounts. More dilute solutions gave greater density catalysts. The resultant precipitate was washed, dried, and sized to two (2) to four (4) millimeters.

(10) The same method was used for preparing the ZnO type catalysts, except it was found that the addition of the nitrate solution to the soda solution instead of the normal method gave increased liquid hydrocarbon yields.

(11) An alternate method for preparing thoria catalysts, and the one which gave the best yields, was to make sodium aluminate and then precipitate with sulphuric acid. Thorium hydroxide precipitate was also made, and these two ppts., were washed separately and mixed while wet. They were then air dried at one hundred (100) degree centigrade and ground to normal size.

(B) Aromatic Synthesis

(1) Aromatics were successfully synthesized by the use of Cr, Mo. Th oxides as catalysts. Five (5) to ten (10) percent K_2CO_3 was added to reduce carbon formation. It also reduced activity. A CO/H_2 ration of 1:1 was used, at thirty (30) atmospheres and five hundred (500) degrees centigrade. Any higher temperature or pressure gave excessive carbon formation on the catalyst, while

2. CONCLUSIONS AND RECOMMENDATIONS

The development of the Fischer-Tropsch process as a producer of iso-paraffins, and thus a source of high quality aviation and automotive fuels, opens the way for it to become the most versatile of all synthetic fuel processes. It would then be capable of producing products which range all the way from high quality diesel fuels and lubricants to excellent aviation gasoline. No other process could make such a claim. It is therefore recommended that this information be made available to all interested agencies, and that the work of Dr. Pichler and Dr. Koch of KWI, which is still continuing at the Institut be closely followed in order to keep American technology as well informed as possible.

3. DETAILS OF SHIPMENTS

Small samples of the thoria-alumina and the ZnO-Al_2O_3 catalysts used in iso-paraffin synthesis are being forwarded to Bureau of Ships (Code 341) on Consignment Tag No. 3655. Under the same consignment is also being shipped small samples of n-octane, n-nonane, and n-decane for use in the standardization of mass spectrographic analysis procedure.

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