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APPENDIX D.

ABSTRACTS OF PATENT APPLICATIONS

RELATING TO THE

FISCHER TROPSCH PROCESS

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Ruhrchemie
R-104584 IVD/120

Filed 20 Feb., 1939

To make products of lower molecular weight and higher olefin content the hydrogenation of CO is carried out with recycling of the product gas after separation of condensibles by cooling and charcoal absorption. With a cobalt catalyst at 200-230°C, a recycle ratio of 3:1 to 10:1 is preferred. A relatively high pressure, 3-10 atm., and high temperatures 200-230°C, can be used. The resulting gas and gasoline is stated to be about 75% olefinic and 55% of the product is in the C₂-C₄ range.

Ruhrchemie
R-104876 IVD/120

Filed 28 Mar., 1939

The hydrogenation of CO is carried out by passing synthesis gas into a suspension of finely divided catalyst in a suitable oil, preferably with mechanical agitation to distribute the gas, and simultaneously introducing a liquid such as water, which vaporizes under the reaction conditions to control the temperature. For example, 1270 gms of Co-ThO₂-MgO- Kieselgur catalyst containing 400 gms. Co is suspended in 15 litres of oil boiling from 240°-300°C. Synthesis gas containing 1 Co:2H₂ is introduced at a rate of 2.5 litres per gm Co per hour, and a pressure of 10 atm. is maintained in the reaction. The synthesis starts at 190°C and the temperature is gradually raised to 210°C as water is introduced to maintain this temperature. The contraction of synthesis gas amounts to 85% and the yield of liquid and solid hydrocarbons amounts to 172 gm/m³. The liquid product contains 90% boiling up to 300°C and having an olefin content of 20%.

Ruhrchemie
R-104999 IVD/120

Filed 15 Apr., 1939

Preparation of synthesis catalysts by precipitating from sulfate instead of nitrate solution and activating by washing with alkali carbonate or hydroxide solution. For example, a catalyst containing 100 parts Co, 10 parts Mg O, 5 parts ThO₂ and 200 parts kieselguhr is prepared from a solution containing 40 gms/liter of Co in the form of sulfate. The precipitate obtained by addition of "soda" is washed first with water (1 liter per 25g Co) then with n/20 (NH₄)₂ CO₃ (1 liter per 25g Co) and finally with water (1 liter per 25g Co).

R-105297 IVd/120

Filed 24 May, 1939

Increasing production of high molecular weight hydrocarbons by using a catalyst on a support of very low bulk density. Low temperatures (160-180°C) low space velocity (4 liters/hr/kg catalyst) elevated pressure (10-20 kg/sq.cm) and high cobalt content (over 100 gm. cobalt per liter of catalyst) are recommended with a catalyst support consisting of uncalcined magnesia or low density kieselguhr.

R-105508 IVd/120

Filed 24 June, 1939

Process and apparatus whereby more uniform flow is maintained through a bed of synthesis catalyst by supplying the synthesis gas through a valve or orifice causing a considerably greater pressure drop than the catalyst bed itself.

R-105615 IVd/23b

Filed 7 July, 1939

Preparation of high anti-knock fuels by heating a Fischer-Tropsch product with a small quantity, about 10%, of the bituminous components of hard coal or brown coal, freed from ash, and preferably under pressure and in the presence of a catalyst and hydrogen. Specifically a Pott-Brosch coal extract is mixed with Fischer-Tropsch product boiling from 200-250°C and passed over a molybdena catalyst with hydrogen at 480-500°C under 80 atm pressure, whereby 70 octane gasoline is obtained. The unconverted kogasin is recycled.

• Braunkohle-Benzin A.G.
185 130 IVd/120

Filed 3 Nov. 1938

Controlling the temperature in the catalytic hydrogenation of carbon monoxide by carrying out simultaneously over the same catalyst an endothermic reaction, specifically the catalytic cracking of alcohols and preferably of isobutyl alcohol.

Ruhrchemie
R-103450 IVd/120

Filed 1 Oct., 1938

Reducing catalysts for hydrogenation of carbon monoxide with hydrogen containing less than 2.5 gms oxides of carbon and less than 1 gm water vapor per cubic meter to get faster reduction and a more active catalyst.

Ruhrchemie
R-103507 IVd/12m

Filed 8 Oct., 1938

In recovering thorium the iron content is minimized by dissolving the iron-thorium slurry with sulfuric acid, adding potassium sulfate to precipitate potassium thorium sulfate and decomposing the latter with sodium carbonate in the presence of

enough additional potassium sulfate to maintain the ratio of K to Na sulfate greater than 1:1. The potassium thorium sulfate is washed with saturated potassium sulfate until the wash liquor contains only traces of iron and then the double salt is "cooked" (under conditions not specified) with the sodium carbonate-potassium sulfate mixture to make thorium hydrocarbonate which contains less than 0.3 parts Fe_2O_3 per 100 parts ThO_2 .

Improvement on R102874 IVd/12m.

Ruhrchemie

R103605 IVb/12m

Filed 24 Oct., 1938.

Improvement on R103507 IVb/12m consisting in treating the washed potassium thorium sulfate with an excess of sodium carbonate to redissolve the initially formed thorium hydrocarbonate as alkali thorium double carbonate and heating this solution to $90^\circ C$ whereby colloidal iron hydroxide is precipitated, together with a small amount of cobalt which may be recovered by recycling. Sulfuric acid is added to the solution to precipitate thorium hydrocarbonate (free from iron) which is filtered out and washed with water. HCl may be used for this precipitation and the solution may be cooled to precipitate alkali sulfate for reuse.

Ruhrchemie

R103713 IVd/12 o

Regenerating synthesis catalyst in situ by continuing hydrogenation after completing wax removal but with increasing temperature. For example treating for 2.5 hrs at $200^\circ C$ with a mixture containing 25% N_2 and 75% H_2 ; raising the temperature to $350^\circ C$ during the period of $\frac{1}{2}$ hr and treating at this temperature for $\frac{1}{2}$ hr; treating $\frac{1}{2}$ hr at $400^\circ C$ and finally at 2 hrs at $450^\circ C$. Original activity is stated to be restored by this procedure.

Ruhrchemie

R103712 IVd/12 o

Filed 7 Nov., 1938

Used synthesis catalyst is subjected to oxidation under unspecified conditions except "elevated" temperature prior to regeneration with hydrogen, whereby the regeneration is said to proceed more rapidly and effectively.

Ruhrchemie

R103980 IVd/12 o

Filed 6 Dec., 1938

Kieselguhr to be used as a synthesis catalyst support is treated with a relatively volatile acid such as HCl or HNO_3 to remove inorganic impurities and is then oxidized below the sintering temperature to remove organic matter and the remaining traces of acids. Alternatively the metals may be removed as bicarbonates by blowing CO_2 through a suspension of Kieselguhr, after which the Kieselguhr is washed, dried, and calcined 1 hour at $550^\circ C$.

Ruhrchemie

Filed 7 Nov. 1938.

R103714 IVd/12 o

Synthesis catalysts are regenerated in situ by removing paraffin and then treating at an elevated (not specified) temperature with hydrogen passed at high velocity, preferably 1000 cubic meters per hour per square meter cross section. The hydrogen can be recirculated if the CO and CO₂ content is kept below 2.5 gm per M³ and H₂O less than 1 gm per M³. Activity attained this way is stated to equal that of a reworked catalyst.

Braunkohle

Filed 23 Aug. 1938.

B184414 IX/421.

A thermocouple with the leads extending in opposite directions from the junction to avoid the problems of electrical insulation etc. associated with parallel leads. For measuring the temperature along the center of a vertical reaction tube the ends would pass through stuffing boxes at the top and bottom of the tube so that the junction could be raised or lowered as desired.

Brabag

Filed 31 Jan. 1938.

B181705 IVd/12 o

Addition to B 178085 IVc/12 O carrying out exothermic reactions such as Fischer-Tropsch synthesis with such a large percent of inert gas in the charge gas that the entire heat of reaction can be carried out as sensible heat of the effluent without harmful temperature rise. No data given.

Brabag

B181885 IVd/23b

Cracking heavy hydrocarbons over catalysts which serve at lower temperatures for the synthesis of hydrocarbons from CO and H₂. Such a catalyst which is spent for synthesis can be used for cracking. The oil to be cracked may be vaporized or atomized with H₂. A cracking temperature of 300-350°C is suggested.

Brabag

Filed 19 Feb. 1938

B182020 IVd/12 o

Pretreating a synthesis catalyst with synthesis gas containing NH₃ for about 20 min. at 185°C. Longer catalyst life is stated to result.

Brabag

Filed 15 Mar. 1938.

B182388 IVd/12 o

Fresh catalyst, preferably blanketed with CO₂ when charged to the oven, is wet with synthesis product, at least in the top part of the oven, to minimize the tendency to excessive reaction and harmful overheating of the fresh catalyst when first put into service.

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Brabag
Bl82389 IVd/12 o

Filed 15 Mar. 1938.

Extracting paraffin from synthesis catalyst by supplying vapors of a solvent, preferably synthesis oil, of such a boiling point that condensate therefrom is formed and flows down through the catalyst to extract the wax at a temperature above its melting point.

Brabag
Bl83662 IVd/23b

Filed 25 June 1938.

To avoid fog formation in condensing oil from synthesis oven effluent by spraying with water, vapors of the oil condensate, or of some oil miscible with the condensate, are combined with the effluent ahead of the water spray.

Ruhrchemie
RI02874 IVb/12m

Filed 1 July, 1938.

In the reworking of spent synthesis catalysts the primary Na_2CO_3 precipitate containing Th and Fe is dissolved in H_2SO_4 . Th is precipitated as thorium potassium sulfate by K_2SO_4 , this is separated and washed and then converted to thorium hydrocarbonate by digestion with concentrated Na_2CO_3 solution.

Ruhrchemie
RI02909 IVd/12 o

Filed 20 July, 1938.

Making relatively light products from the hydrogenation of CO by using a catalyst containing not more than 33% by weight of active metal and operating at relatively high temperatures (235-240°C with Co) and high space velocities (up to 9m^3 synthesis gas per Kg Co per hr).

Ruhrchemie
RI02756 IVd/23b

Filed 2 July, 1938.

The octane number of benzine from the hydrogenation of CO is improved (from 5 to 10 points) by passage over material of high surface area such as silica gel, active carbon, acid treated clay, etc. at 180-200°C, apparently as a result of isomerization.

Ruhrchemie
RI03371 IVb/12n

Filed 20 Sept. 1938.

The calcium impurity in cobalt nitrate solution prepared in reworking catalysts is precipitated by a soluble fluoride in the presence of added magnesium (nitrate). Any excess of soluble fluoride over that required to precipitate Ca will precipitate as Hg F_2 , thus leaving no fluoride in solution to precipitate inactive cobalt fluoride when Na_2CO_3 is added.

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Ruhrchemie
R101215 IVd/12 o
Addition to R97521 IVc/12 o

Filed 6 Jan. 1938.

Before discharging spent synthesis catalyst for reworking it is treated with inert gas such as steam at temperatures above 300°C and with a velocity of at least 1 meter per second to sweep out remaining oil and wax.

Ruhrchemie
R101219 IV/40a

Filed 7 Jan. 1938.

In reworking cobalt synthesis catalysts the iron-thorium sludge is dissolved in acid and then treated with excess sodium carbonate at about 40-50°C to precipitate iron as hydroxide and keep thorium in solution as sodium thorium carbonate which is subsequently hydrolyzed to hydrocarbonate.

Ruhrchemie
R101354 IVd/12 o

Filed 21 Jan. 1938.

Spent catalyst, after being freed from paraffin, is discharged and reworked by initial solution of active components in ammonium carbonate solution instead of acid. This is stated to facilitate elimination of impurities but details are not given.

Ruhrchemie
R101389 IVb/26d

Filed 25 Jan. 1938.

Organic sulfur compounds in gases are converted to H₂S by heating the gas, preferably with added O₂ and steam rapidly to above 400°C and digesting at this temperature in the absence of a catalyst for a considerably longer time than required for heating. Final heating is preferably accomplished by partial combustion to prevent trouble due to deposition of solids on indirect heating surfaces.

Brabag
B.182409 IVd/12 o

Filed 16 Mar. 1938.

In the hydrogenation of CO with a Co catalyst longer life is obtained if steam is added to the synthesis gas during initial operations according to the following schedule for example:

0 to 20 hrs.	2 - 2.5 vol.% steam
20 to 30-50 hrs.	0.7 - 1.5 vol.% steam
30-50 to 100-300 hrs.	0.1 - 0.2 " " "
After 300 hrs.	enough to make dewpoint 20-25°C

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Brabag
B184450 IVb/12g

Filed 27 Aug. 1938.

Catalyst ovens or tubes are emptied of catalyst by suddenly applying a gas pressure of 5-20 atm, preferably after wetting the pressure side of the catalyst bed with a liquid.

Brabag
B178627 IV/26d
Addition to B175954 VI/26d

Filed 29 May, 1937.

A catalyst containing an oxidizing salt such as sodium nitrite on a support such as active carbon is used for organic sulfur removal (as covered by 175954) and when spent for this purpose is used to convert organic sulfur to H₂S, which can be removed by well known methods.

Brabag
B178964 IVc/12 o

Filed 24 June, 1937.

Using the relative CO₂ content or density of end gas in comparison with charge gas as a guide for adjusting operating conditions, particularly coolant supply.

Brabag
B179047 VI/26 d

Filed 29 June, 1937.

Carrying out the catalytic removal of organic sulfur compounds from gases by plural stage operation with a higher temperature in the last stage than in the first.

Brabag
B179612

Filed 14 Aug. 1937.

Synthesis gas from brown coal is freed from resin forming constituents, independent of desulfuring, by cracking in a copper stove or adsorbing on active carbon, brown coal, coke, or bleaching earth.

Brabag
B179862

Filed 8 Sept. 1937.

Oil from the Fischer Tropsch is neutralized by percolation through bleaching earth at about 150°C.

Brabag
B179863

Filed 8 Sept. 1937

Oil from Fischer Tropsch synthesis is neutralized by contacting with iron oxide in the form of gas purification "Masse" or

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"Lautmasse" and the like, at 120-150°C and regenerating the mass by treatment with steam or hot water at a higher temperature (175°C).

Brabag

B177992 IVc/12 o

Filed 6 Apr. 1937

Using for the Fischer Tropsch process a synthesis gas prepared from coal for coke and removing residual hydro-carbons from the synthesis gas by active charcoal or by contact with hot sulfuric acid or by cooling sufficiently to condense the hydrocarbons.

Brabag

B178085 IVC/12 o

Filed 14 Apr. 1937.

Diluting synthesis gas with reaction products so that the heat of reaction can be carried out as sensible heat of the mixture without excessive temperature rise.

Brabag

B175954 IVb/12c

Filed 23 Oct. 1936.

Desulfurizing synthesis gas by contact with an oxidizing agent such as a nitrite, chlorate, permanganate etc. on a support such as active carbon silica gel etc. at a temperature of about 80°C.

Krupp

K147143 IVb/12g

Filed 5 July 1937.

Reactor for the Fischer-Tropsch process in which the cross section of the catalyst bed decreases from inlet to outlet according to the contraction in volume of the reacting gases.

Krupp

K148919 IVb/12g

Filed 20 Dec. 1937.

Carrying out Fischer-Tropsch synthesis (or other reactions with large heat effects) in a plurality of stages and introducing between stages sufficient cold charge gas to hold the desired temperature in the subsequent stage.

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