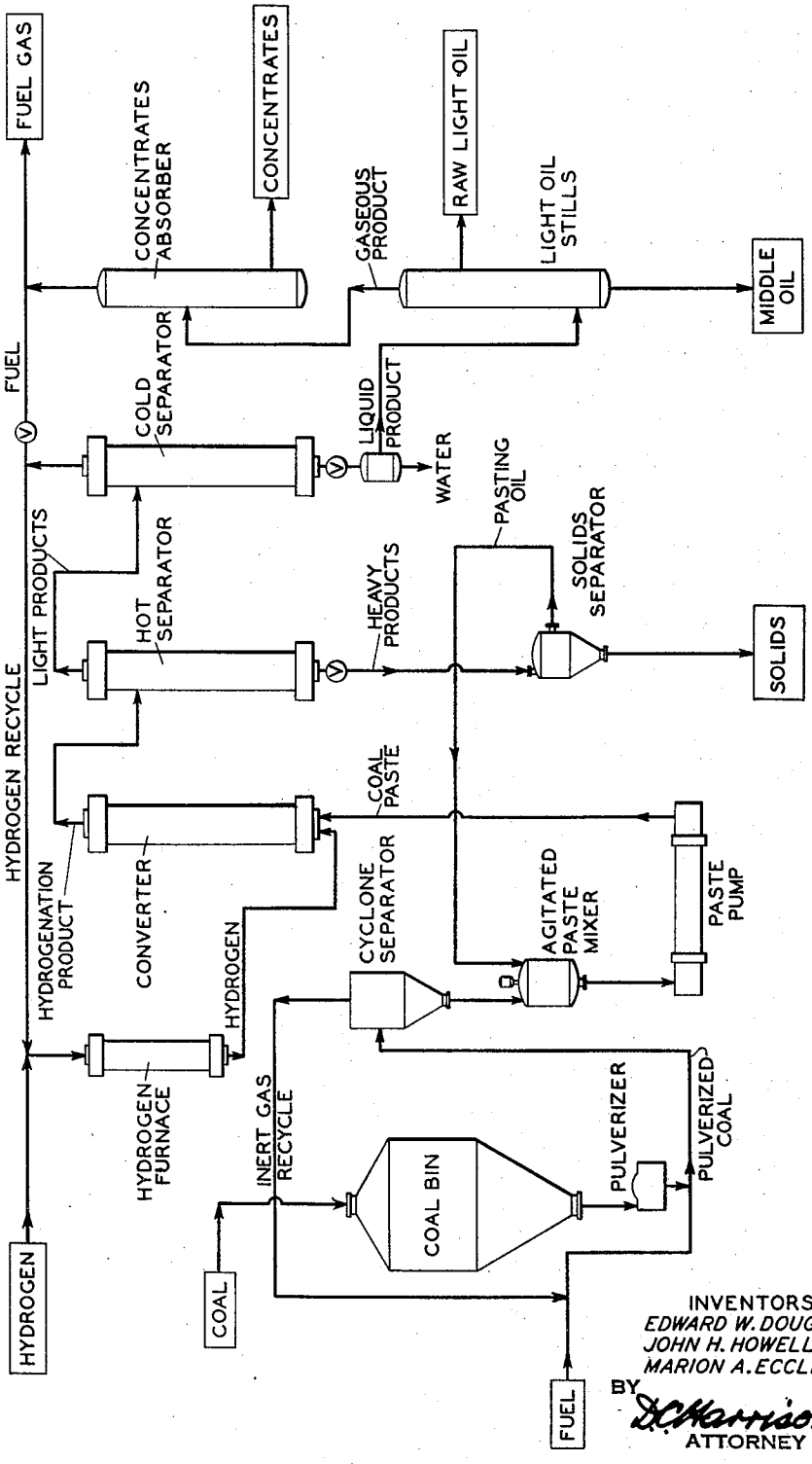
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COAL HYDROGENATION PROCESS

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COAL HYDROGENATION PROCESS

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This invention relates a fundamental improvement in the process of coal hydrogenation wherein the costs of the equipment required are greatly reduced and the efficiency of the process is increased.

The coal hydrogenation process, in its present stage of development, starts with the preparation of a coal paste. To make the paste, finely pulverized coal is blended with a pasting oil, which is a heavy oil fraction recycled from the hydrogenation process. According to present practice, about equal parts of the pulverized coal and pasting oil, together with a small amount of catalyst, are blended at about 100° to 150° C. in a steam-jacketed mixer. The blended mixture is held in storage in heated tanks, from which it is pumped by high pressure reciprocating pumps up to the pressure of the converter which in recent practice is about 10,000 p. s. i. One of the most difficult steps of the present process then occurs and involves heating the coal paste at converter pressure up to 425° to 445° C. This pre-heating of the coal paste presents several severe problems. In the first place, the coal paste has a low coefficient of heat transfer which necessitates that a large area of heating surface be employed. This greatly increases the amount of expensive high pressure equipment required. Also, there is danger of the paste becoming coked because of hot spots forming in the heat transfer tubes. In addition, heat is transferred to the paste from the outside wall of the coal paste pre-heater and a thermal gradient in this direction increases the stress on the pre-heater walls.

Another problem which must be overcome in the design of the coal paste heater arises from the characteristics of the paste on heating. At higher temperatures the coal particles begin to swell and the coal paste begins to increase markedly in viscosity. The swelling of the coal paste is also related to the time at which it is held at a given temperature, the degree of swelling increasing with the duration of the heating until coking eventually results, if the temperature is within the coking range. To overcome this swelling of the paste, and to prevent coking and formation of refractory bodies in the paste which are difficult to hydrogenate, one form of present practice involves injecting hydrogen and additional pasting oil at a point in the pre-heater just prior to the section where a temperature of 315° C. is reached. Although this expedient is successful in preventing immobility of the paste and in avoiding coking, the dilution of the paste in this manner decreases the amount of coal which can be hydrogenated in a given size converter, and increases the amount of oil which must be recycled through the process.

According to this invention, the pulverized coal and the pasting oil are heated separately to a high temperature. By pre-heating the pasting oil, independently of the coal, no anomalous viscosity effects are obtained and the viscosity of the pasting oil decreases normally with the temperature. Likewise, by heating the pulverized coal in the absence of the pasting oil, coal particles are not surrounded by a viscous oil which would tend to form a gelatinous paste. Upon mixing the hot pulverized coal and the hot pasting oil a semi-colloidal dispersion or partial solution of the coal in the oil occurs leading to pastes sufficiently fluid for pumping. Such pastes may be then pumped under pressure together with the necessary hydrogen directly to the hydrogenation converter without further heating of the paste. In order to achieve the formation of a fluid paste, it is necessary that the coal and the pasting oil be heated to such a degree that the mixed paste will have a minimum temperature above that where excessive viscosities are encountered. Thus, it is necessary that the mixed paste have a minimum temperature of 300° C. and it is preferable that the paste have a temperature in the range of 325° C. to 400° C. The temperature to which the oil and coal are heated individually need not be a minimum of 300° C., but each may be heated individually to a temperature so that, on mixing, the temperature of the mixture will be at least 300° C. We have further found that the coking reaction is quite slow in this temperature range, so that the pastes may be kept at 325° to 400° C. for the time required for mixing, storage and transport to the hydrogenation converter.

By the present method of mixing, coal pastes containing in excess of 50% coal by weight, for example 65% to 75%, may be prepared in a fluid state, whereas the prior practice is limited by the viscosity of the paste to coal concentrations of 40 to 50%. The use of more concentrated coal pastes permits a proportionate reduction in the size of the hydrogenation equipment required for a given throughput of coal. Since the converters must be built to withstand pressures of 10,000 p. s. i. or higher at inside temperatures of 480° C. to 540° C., any reduction in their size represents an important economy.

A still greater saving results when the coal paste is prepared by separately heating the coal and pasting oil and then mixing them in that the paste pre-heaters required in the conventional process are eliminated. Since the paste pre-heaters represent an appreciable fraction of the investment required for a conventional coal hydrogenation plant and also require considerable maintenance, it is apparent that their elimination greatly reduces the cost of converting coal to liquid products by the hydrogenation process. The pasting oil required for mixing with the pulverized coal may be recycled in a heated condition from the hydrogenation and separation process, so that the only heat required for pre-heating the feed to the hydrogenation converters is that needed for the coal and the hydrogen. Hydrogen gas has excellent heat transfer characteristics so that it may be heated readily in known types of equipment. The temperature to which the hydrogen is heated may be above or below reaction temperature depending on the heat balance in the converter, including the heat of reaction. To prevent the accumulation of refractory bodies in the pasting oil, it is desirable but not essential to distill the oil before recycling it to the paste mixers. When distilled oil is recycled, some pre-heating of the oil may be required, depending on the distillation temperature.

The pre-heating of the coal prior to mixing with the hot pasting oil has not heretofore been practiced, and the finding that pulverized coal could be heated up to temperatures of 325° to 400° C. without coking or agglomeration of the coal particles was an important discovery contributing to the success of the present process. In small scale operation to demonstrate the process, it is possible to pre-heat the pulverized coal in an electrically heated autoclave equipped with an agitator prior to adding the hot pasting oil, but in full scale industrial operation other means of pre-heating the coal are desirable. It has been found that the pulverized coal may be rapidly

heated from storage temperature up to 325° to 400° C. by suspending the coal in hot inert gases from a combustion process until the coal particles are heated to the desired temperature, and then separating the suspended hot coal particles from the inert heating gas by suitable equipment, such as a cyclone separator. It has been found that the hot coal particles do not agglomerate when collected by such equipment and that they may be handled as a powder for feeding into a mixer to form a paste with the hot pasting oil. This coal heating process is further described in a copending application, Serial No. 256,301, filed November 14, 1951, by R. Gorman, R. G. Edmonds, and E. W. Doughty, entitled A Process for the Heating of Coal.

In the figure a flow sheet is shown giving the essential elements of a coal hydrogenation process in which the paste is prepared by the improved method of this invention.

In the flow sheet, coal enters the process and is stored in a bin, from which it passes to a pulverizer. The pulverized coal is picked up in a hot stream of inert gas which is kept at the heating temperature by combustion of the required amount of fuel gas. The powdered coal is heated by this hot stream of gas up to 325° to 400° C. and then passes to a cyclone separator where it is recovered from the inert gas which is recycled. A purge is taken from this recycle to maintain it at an approximately constant volume. The hot coal powder passes from the separator to a paste mixer equipped with an agitator where it is mixed at a temperature of 325° C. to 400° C. with hot pasting oil. The required pasting oil may be recycled from the separated hydrogenation products. A catalyst, such as a tin compound, is usually incorporated with the paste in the mixer. The mixing of the paste can be carried out in a continuous manner by feeding the hot coal and the hot oil into an agitated mixer, and continuously withdrawing paste from the mixer.

The paste is pumped from the mixer by a paste pump up to reaction pressures of 2000 to 10,000 p. s. i. and passes to the converter. Hydrogen is introduced in the system under reaction pressure and heated above or below reaction temperatures depending on the thermal requirements of the system in a suitable hydrogen furnace from which it passes together with the coal paste to the converter where a known chemical reaction occurs between the coal and the hydrogen at temperatures of 450° to 550° C. Heat released in the reaction may be removed by known practices, but the introduction of a hot paste below the reaction temperature is advantageous. Thus, part of the heat of the reaction will be absorbed in bringing the paste feed up to reaction temperature, particularly if good circulation of the reactants is obtained in the converter.

The hydrogenation product passes to a hot separator where the heavy products, i. e. the heavy pasting oil and solids are removed, and the separated heavy products are treated to separate the solids, as by filtration or centrifuging. The hot pasting oil freed of solids is recycled to the paste mixer. Depending on the yields of the various fractions desired, some of the pasting oil may be withdrawn as a heavy product. The light products pass from the hot separator to the cold separator where the liquids are separated from the hydrogen, methane, and other uncondensed constituents, part of the hydrogen-methane fraction being recycled and part being withdrawn as fuel gas.

The liquid product from the cold separator, after being decanted from water, passes to a light oil still, where it may be fractionated into a gaseous product, a raw light oil and a middle oil. The gaseous products pass to a concentrates absorber where C_2–C_5 hydrocarbons may be separated as concentrates, and the remainder of the gaseous product withdrawn as fuel gas.

The following example will illustrate the preparation of coal paste by the improved method.

Pulverized coal was introduced into an electrically heated autoclave equipped with an agitator, and heated. Pasting oil was heated in a separate vessel and blown with nitrogen pressure into the autoclave at a temperature of 350° C. Two runs were made at coal concentrations of 50 and 60% in the pastes respectively. In both cases, a fluid mixture was obtained at the autoclave temperature and there was no visual evidence of coking. Samples of the hot paste when cooled set to a hard, brittle solid similar to hard asphalt. When reheated to approximately 250° C., the solids re-melted in a manner similar to asphalt or pitch. The first sample, at 50% concentration, was mixed for 14 hours during which time the temperature fell from 350° C. to 260° C.; of the total time, only 25 minutes were at a temperature of 300° C. or higher. The second sample, at 60% concentration, was agitated for approximately two hours, during which time 45 minutes were occupied in cooling the batch from 350° to 300° C.

Hydrogenation tests in a static bomb were run on both the 50 and 60% coal pastes thus mixed at an initial hydrogen pressure of 2500 p. s. i. for one hour at 480° C. to determine whether any carbonization or other adverse change occurred during the long contact time at elevated temperatures. For comparison, a control run was also made under the same conditions in which a 50 percent coal paste, prepared from the same coal and oil used in making the hot mixed sample, was charged to the bomb without pre-heating. In carrying out the test runs, the hot mixed pastes were allowed to cool prior to hydrogenation. In each run, 200 grams of the paste was charged to the bomb which was then filled with hydrogen at 2500 p. s. i. at 50° C. The contents of the bomb were then heated for 1.5 hours until a maximum temperature of 480° C. was reached, at which point the pressure in the bomb was about 3700 p. s. i. The charge was held at this temperature for one hour, at which time the pressure was about 2800 p. s. i. The bomb was then cooled and the products analyzed.

In the control run, the conversion of coal to gaseous and liquid products was 93%, whereas the conversions to liquid and gaseous products of the 50% and 60% coal pastes which were hot mixed were 92% and 93% respectively. The liquid products of the hydrogenation step contained chemically combined hydrogen; the carbon to hydrogen weight ratio being 12.9 for the control run, and 13.5 and 12.3 respectively for the 50% and 60% coal pastes prepared by hot mixing.

These data indicate that preparation of the coal paste by separate heating of the coal and oil, and then mixing, does not impair the effectiveness of the hydrogenation step in converting the coal to liquid and gaseous hydrogenation products.

What is claimed is:

1. The process of reacting hydrogen with coal to form hydrogenation products which comprises separately heating pulverized coal, mixing the heated pulverized coal with hot pasting oil to effect a distribution of heat between the oil and coal whereby the temperature of the mixture is at least 300° C. and dispersing the coal in the oil to form a fluid paste capable of being pumped, directly mixing the hot paste with hydrogen under pressure to form hydrogenation products and recovering the said hydrogenation products.

2. The process of reacting hydrogen with coal to form hydrogenation products which comprises separately heating pulverized coal, mixing the heated pulverized coal with hot pasting oil to effect a distribution of heat between the oil and coal whereby the temperature of the mixture is 325° C. to 400° C. and dispersing the coal in the oil to form a fluid paste capable of being pumped, directly mixing the hot paste with hydrogen under pressure to form hydrogenation products and recovering the said hydrogenation products.

3. Process as claimed in claim 2 in which the paste contains up to 75% coal by weight.

4. Process as claimed in claim 2 in which the paste contains in excess of 50% coal by weight.

5. Process as claimed in claim 2 in which the paste contains from 50% to 60% coal by weight.

6. The process of reacting hydrogen with coal to form hydrogenation products which comprises separately heating pulverized coal, mixing the heated pulverized coal with hot pasting oil to effect a distribution of heat between the oil and coal whereby the temperature of the mixture is 325° C. to 400° C. and dispersing the coal in the oil to form a fluid paste capable of being pumped, directly mixing the hot paste with heated hydrogen under pressure and causing the hydrogen to react with the coal paste at a temperature higher than the paste mixing temperature whereby at least part of the heat of the hydrogenation reaction is utilized in heating the coal paste to reaction temperature, and recovering the hydrogenation products.

7. The process of reacting hydrogen with coal to form

hydrogenation products which comprises separately heating pulverized coal, mixing the heated pulverized coal with hot pasting oil to effect a distribution of heat between the oil and coal whereby the temperature of the mixture is 325° C. to 400° C. and dispersing the coal in the oil to form a fluid paste capable of being pumped, directly mixing the hot paste with hydrogen under pressure at a hydrogenation temperature of about 450° C. to 550° C., to form hydrogenation products, separating a pasting oil fraction from the hot hydrogenation products formed, and returning said pasting oil in a heated condition to the coal mixing operation.

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