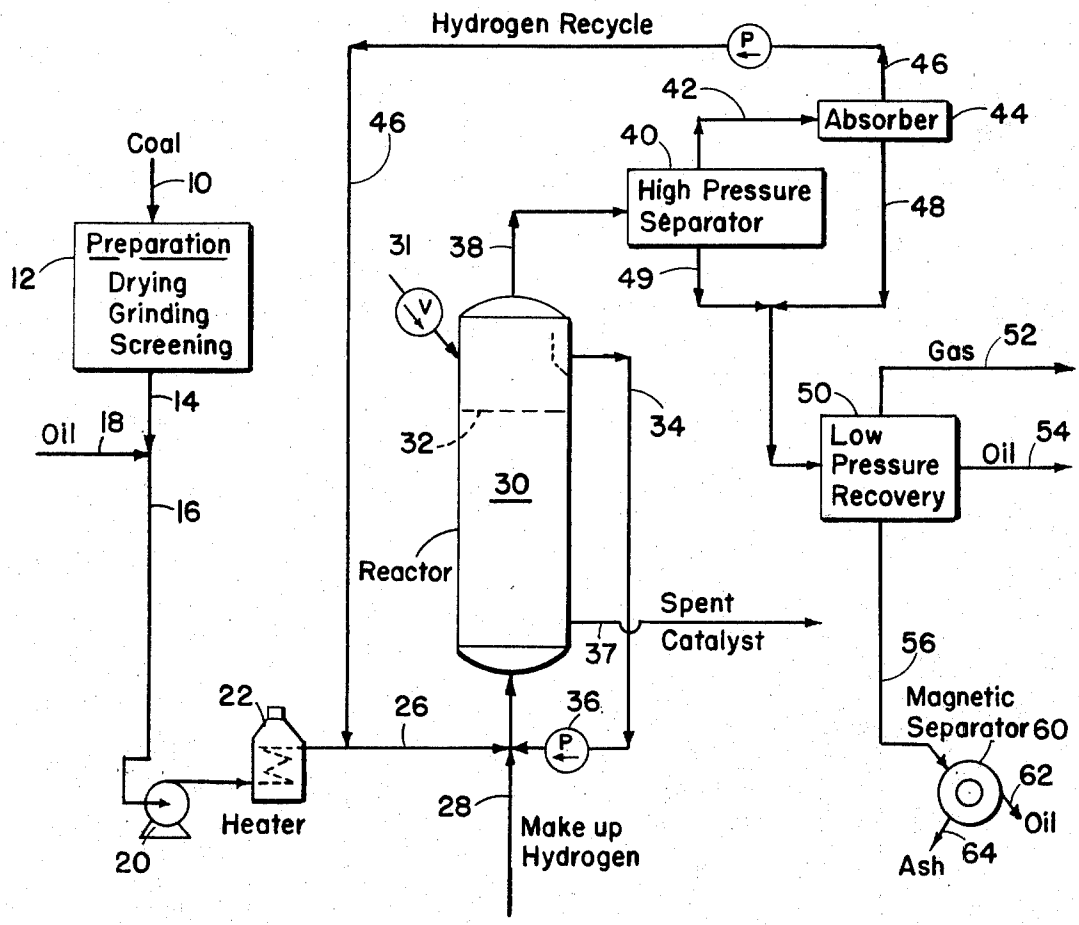
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SOLIDS REMOVAL FROM HYDROGENATED COAL LIQUIDS

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SOLIDS REMOVAL FROM HYDROGENATED COAL LIQUIDS

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ABSTRACT OF THE DISCLOSURE

Better than fifty percent of the ash and associated solids from a coal-derived oil, such as a hydrogenated coal product, are removed by magnetic separation. The ash and associated solids have been rendered magnetically susceptible by prior hydrogenation treatment.

BACKGROUND OF THE INVENTION

As described in the U.S. Pat. No. 3,519,555, the hydrogenation of coal to more valuable products (both liquid and gas) utilizing relatively low reactor pressures and achieving better than 80 percent conversion of the coal thereby producing in the order of four barrels of oil per ton of coal makes available for the first time a nearly inexhaustible fuel source for commercially competitive fuels.

It is recognized, however, that such liquid (coal-derived oil) contains the ash and unconverted solids which frequently amount to 15 to 20 percent of the coal. It is quite apparent that such solids material must be removed from the oil if it is to have commercial value, and often this removal carries with it some additional fraction of the liquid product.

The usefulness of removing metallic contaminants from coal and ores by magnetic means is, of course, well known and there are many processes available and substantial prior patent art. For example, it is well known in the water washing of coal to utilize magnetic separation for removing metal such as tramp iron. In the Leeman patent, U.S. 2,998,882, it is suggested for example that magnetic separations of both coarse and fine particles can be accomplished to remove magnetite. In the later patent to Ergun U.S. 3,463,310, it is suggested that electromagnetic heating of the iron particles in coal tends to convert them to a magnetic form. He proposes to use microwave energy to convert pyrites to pyrrhotite, magnetite, etc. before magnetic separation. As pointed out, this avoids the need of the high conversion temperatures of 360–600° C. formerly thought necessary, and which would tend to undesirably remove coal volatiles. Utilization of energy frequencies of the order of 10^6 Hz. or greater for the volumes of coal in commercial operations is considered uneconomical. However, the removal of known magnetic particles even in liquid-coal mixtures has given no suggestion of applicability to coal solids in coal-derived liquids generated by hydrogenation.

SUMMARY OF THE INVENTION

I have now found, however, that coal-derived oil from the hydrogenation of coal by the expanded (ebullated) bed reaction process hereinbefore discussed, while containing solids including ash and unconverted coal, if treated by conventional magnetic means can be freed of such solids up to as much as 98 percent. This was completely unexpected as the initial ash is commonly found to be non-magnetic and the extent to which there is any iron present is so small as to render magnetic separation substantially useless. It appears that the prior hydrogenation process influences the ash particles and renders them susceptible to removal by magnetic means.

While I am not certain of the phenomenon, it appears

that the iron in the ash, which is probably originally in the form of ferric sulfide, is converted during the hydrogenation to a reduced form and, in the magnetic field, it serves as a nucleus to carry with it other non-magnetic portions of the ash. A highly beneficial substantially solids-free liquid product is thus obtained.

There is of course a general relationship which exists between the magnetic susceptibility of the coal-derived particulate solids, the temperature and viscosity of the separator bottoms liquid, and the magnetic field strength required for effective separation of the solids therefrom. For particles which are only slightly magnetic, relatively high magnetic field strengths are required to effect a useful separation, particularly if the liquid is moderately to highly viscous. Increased temperature of the liquid and/or use of normally less viscous liquid will permit somewhat lower field strengths to be effectively utilized for particle separation. To achieve useful separations the magnetic field strength for this invention should be at least about 5,000 gauss, and preferably greater than about 10,000 gauss. Also for useful results, the viscosity of the solids-containing liquid as fed to the magnetic separator device should not exceed about 500 centipoise and preferably should not exceed about 50 centipoise.

This liquid viscosity may be adjusted by varying either the liquid composition of the liquid-solids stream, or by varying its temperature, or both. Usual operating conditions for the liquid-solids stream from which the solids are magnetically separated are 400–600° F. temperature and having a liquid viscosity of 2–10 centipoise. The particle size of the ash solids in this liquid-solids stream will usually be smaller than about 200 mesh U.S. Std. sieve series, or smaller than about 75 microns.

While this invention appears to be applicable to various types of hydroconversion processes, wherein at least 50 weight percent conversion is accomplished, I find that the results from ebullated bed continuous hydrogenation process are exceptional, wherein in excess of 80 weight percent conversions are obtained.

DESCRIPTION OF THE DRAWING

The drawing is a schematic view of the relevant apparatus for coal hydrogenation.

DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention will now be described as used with an ebullated bed type hydrogenation process. As shown, a coal such as bituminous, semibituminous, subbituminous or lignite, entering the system at **10** is first passed through a preparation unit generally indicated at **12**. In such a unit it is desirable to dry the coal of substantially all surface moisture and to grind the coal to a desired mesh and then to screen it for uniformity. For our purposes, it is preferable that the coal has a particle size of about 50 mesh (U.S. Std. screen) and finer.

The coal fines discharge at **14** into the transfer line **16** where the coal is blended with a carrying oil indicated at **18** which, as hereinafter pointed out, is conveniently made in the system. To establish an effective transportable slurry, it is found that the ground coal should be mixed with at least about an equal weight of carrying oil.

The coal-oil slurry is pressurized by pump **20** to superatmospheric pressure such as 500–5000 p.s.i. partial pressure of hydrogen, and is then passed through heater **22** to bring the slurry up to a temperature in the order of 750° F. to 950° F., and preferably 800° F. to 900° F. Such heated slurry then discharges into the reactor feed line **26** wherein it is supplied with make-up hydrogen from line **28** as well as recycle hydrogen from line **46**.

The entire mixture of hydrogen and coal-oil slurry then

enters one or more reactors **30**, passing upwardly from the bottom at a rate and under pressure and at a temperature to accomplish the desired hydrogenation. In addition, a hydrogenation catalyst may be added to reactor **30** at **31** in the ratio of about 0.1 to 2.0 pounds of catalyst per ton of coal. Such a catalyst would be from the class of cobalt, molybdenum, nickel, tin, iron and the like deposited on a base of the class of alumina, magnesia, silica, and the like and of a size at least 1/32 inch and more frequently as extrudates in the range of 1/16 to 1/4 inch, i.e., between about 3 and 14 mesh screens of the U.S. Std. scale. It is noted that the catalyst need not be added continuously nor is it required that it be in fine admixture with the coal.

By concurrently flowing streams of liquid and gasiform materials upwardly through a vessel containing a mass of solid particles of a contact material, which may be a specific catalyst as above indicated, and expanding the mass of solid particles at least 10 percent over the volume of the stationary mass, the solid particles are placed in random motion within the vessel by the upflowing streams. A mass of solid particles in this state of random motion in a liquid medium may be described as "ebullated." The characteristics of the ebullated mass at a prescribed degree of volume expansion can be such that a finer, lighter particulate solid will pass upwardly through the catalyst mass, so that the particles constituting the ebullated mass are retained in the reactor and the finer, lighter material may pass from the reactor. The catalyst bed upper level **32** above which few, if any, particles ascend is called the upper level of ebullation.

In general, the gross density of the stationary mass of contact material will be between about 25 and 200 pounds per cubic foot, the flow rate of the liquid will be between about 5 to 120 gallons per minute per square foot of horizontal cross section of the ebullated mass, and the expanded volume of the ebullated mass usually will be not more than about double the volume of the settled mass and preferably greater by at least about 30 percent. A recycle liquid stream **34**, which may be internal or external of the reactor, may be removed above the upper level of ebullation **32**, and recycled by pump **36** to the bottom of the reactor **30** to maintain the desired superficial liquid velocity in the reactor. Spent catalyst may be removed from time to time by drawoff **37**.

Preferred reactor operating conditions are in the order of 800° to 900° F. and about 1000 to 3000 p.s.i. partial pressure of hydrogen. Coal throughput or space velocity is at the rate of 15 to 150 pounds coal per hour per cubic foot of reactor space, so that the yield of unreacted coal as char is between 5 and 15 percent of the quantity of moisture and ash free coal feed. The relative size of the coal and catalyst particles and conditions of ebullation are such that the catalyst is retained in the reactor, while the ash and unreacted char is carried out with the reaction products and the slurry oil solid.

The reactor effluent stream **38** passing to high pressure separator **40** includes some gaseous fractions and is virtually free of solid particles of contact material, although it may contain ash and char in the liquid. From the separator **40**, a gas stream is removed at **42** and then passed to absorber **44**. A hydrogen recycle in line **46** removed from absorber **44** may be returned to the reactor **30** to supplement the hydrogen requirements. A liquid stream from the absorber **44** will be removed at **48** and this is joined with the liquid stream **49** from the high pressure separator **40**. The combined liquid stream is then passed to a low pressure recovery system **50**.

The low pressure separator **50** operates at 500 to 650° F. and permits removal of a high B.t.u. heating value gaseous product at **52** and a solids-free liquid at **54**. A separate bottoms liquid stream containing ash and char is removed at **56**. A portion of the liquid from line **54** may be used as stream **18** to prepare the initial coal-oil slurry.

The solids-oil mixture in line **56**, which usually has an ash concentration in the range of 5 to 15%, temperature of 450° to 600° F. and viscosity of 2 to 10 centipoise, is passed to magnetic separator **60** having a field strength of at least about 5000 gauss. It conveniently and preferably may be a standard rotary or drum type unit having an appropriate magnetizable surface suitably controlled by circuits to energize portions thereof during rotation. By applying the desired magnetic force to liquid stream **56**, the oil portion may be removed at **62** and the magnetic ash portion removed at **64**. Suitable scraper blades as recognized in the industry may be used.

If a very high degree of ash separation is required, the oil stream **62** may be passed to a second magnetic separator (not shown) by which further magnetic particles are removed.

Example

This invention was verified in an experiment performed using a sample of coal-derived separator bottoms liquid containing particulate ash and unconverted coal solids, and designed to be functonally equivalent to actual process conditions. This liquid material was extracted with benzene to dissolve the oil, then the dried particulate material was dispersed in a 6% weight/volume solution of benzene in a glass test tube at room temperature, which was held vertically between the poles of a magnet having a field strength of about 10,000 gauss. After a short time, e.g., about three minutes, the bulk of the particulat solids had settled to the bottom, but some solids remained clinging to the sides of the test tube adjacent the magnet poles. This latter material was removed for chemical analysis, and the procedure repeated. Results using two coal samples are given in the table below:

TABLE

	Weight percent		
	Sample	Sulfur	Carbon
Sample A:			
Original sample		7.35	21.6
1st magnetic fraction	18.0	9.33	20.6
2d magnetic fraction	21.0	8.01	20.4
Residue	61.0	6.61	23.3
Total	100.0		
Sample B:			
Original sample		7.83	19.1
1st magnetic fraction	51.7	8.47	18.9
2d magnetic fraction	31.0	7.57	19.8
Residue	17.3	6.16	22.4
Total	100.0		

These coal hydrogenation solids dispersed in benzene at room temperature comprise a liquid-solids mixture that was chosen to have approximately the same viscosity and to respond to a strong magnetic field in a substantially equivalent manner as the ash and unconverted coal solids dispersed in the actual separator bottoms oil at process temperatures of 450 to 600° F.

Using a new sample of separator bottoms liquid-solids material, a new sample was prepared and several successive magnetic fractions were removed from the benzene dispersion using the above procedure. It was estimated that up to about 98% of the solids material could be removed from the liquid using this magnetic separation procedure.

Thus, these experiments demonstrated that an unexpected and useful separation of these fine ash solids from the separator bottoms oil stream resulting from coal hydrogenation can be made by magnetic means using field strength of at least 5,000 gauss.

On a sample of finely-ground feed coal sized to −200 mesh, it was found that about 98 percent was non-magnetic using the same equipment and technique.

In addition to passing the liquid-containing solids at a suitable temperature (about 500° F.) and a dilution to a viscosity less than about 500 centipoise through a rotary type magnetic separator, so that the accumulated solids can be removed by scraping or demagnetizing, it is alternatively possible to pass the liquid through a magnetic

grid or screen for separation. The accumulated solids can be removed therefrom by washing and/or demagnetizing.

Prior experimentation which yielded the results indicated above on a hydrogenated coal-derived oil resulting from the ebullated bed process leads me to believe that other hydrogenated coal-derived oils are substantially as susceptible to magnetic separation of ash. In such cases, the resulting ash would similarly be of about the same composition and thus susceptible to separation by magnetic means.

What I claim is:

1. In the hydrogenation of coal under liquid phase conditions in a reaction zone at a temperature in the range of 750 to 950° F. and superatmospheric pressure for a time sufficient to convert at least 50 weight percent of the coal to liquid and gaseous products, the improvement in removing ash and unconverted solids from the liquid-solids effluent, which improvement consists in passing the liquid-solids effluent through a magnetic field of at least about 5,000 gauss to attract the magnetically susceptible particles, and recovering a liquid which is substantially solids-free.

2. The process of claim 1 wherein the viscosity of said liquid-solids effluent stream does not exceed about 500 centipoise.

3. The process of claim 2, wherein the magnetic field strength is greater than about 10,000 gauss.

4. The process of claim 3 wherein the ash particles removed are smaller than 200 mesh U.S. Std. screen size.

5. The process of claim 1 wherein the hydrogenation is accomplished in the presence of a particulate hydrogenation catalyst and in which the coal in the presence of a liquid recovered from the process is passed upwardly through the reaction zone under ebullated bed conditions, and the ash concentration is in the range of 5 to 15 weight percent of the coal feed.

6. The process of claim 1 wherein the magnetic field is provided by a drum type magnetic separator.

7. The process of claim 1 wherein the magnetic field is provided by a grid type magnetic separator.

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