

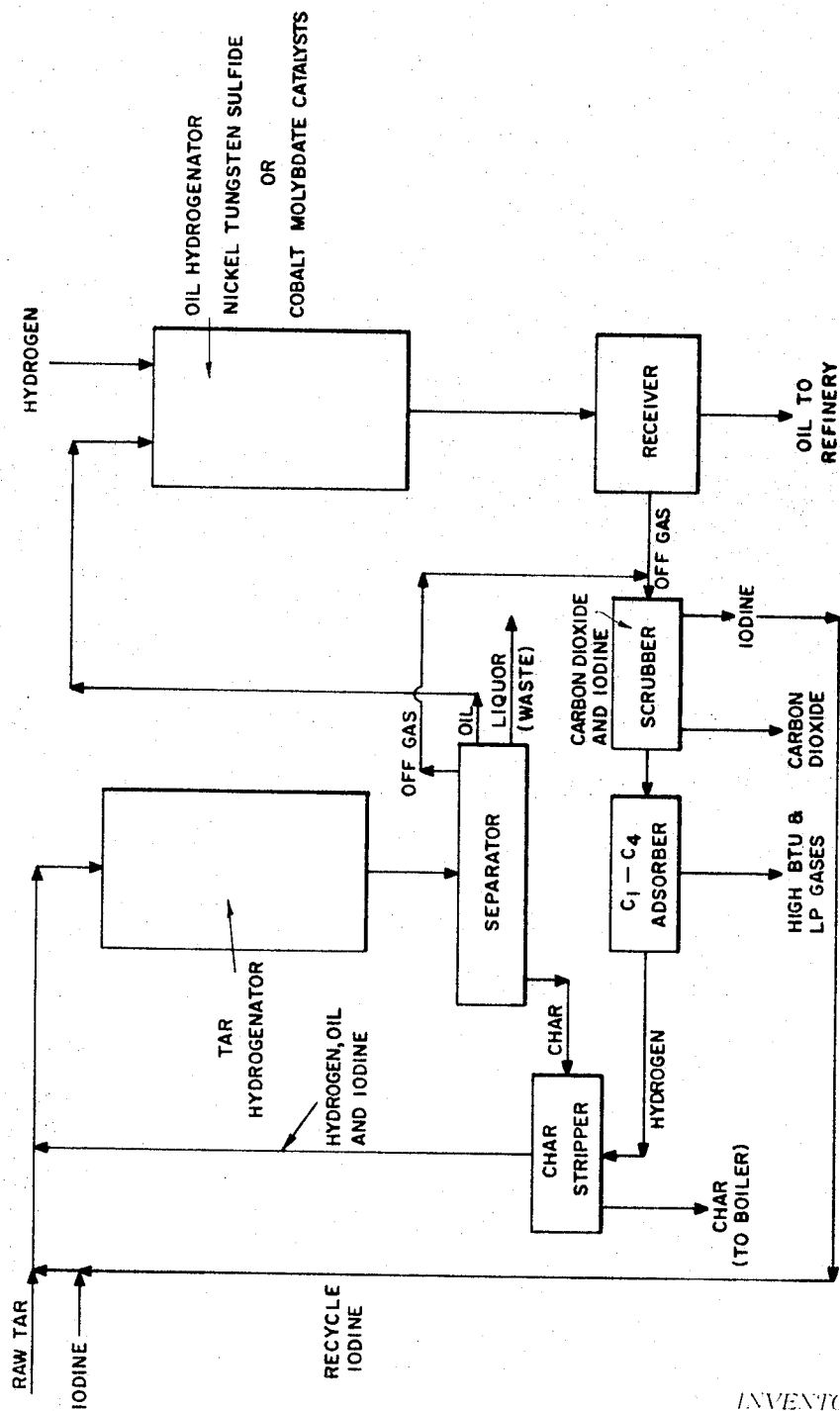
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HYDROGENATION OF COAL TAR

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HYDROGENATION OF COAL TAR

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6 Claims

This invention resulted from work done under Contract 14-01-0001-235 with the Office of Coal Research in the Department of the Interior, entered into pursuant to the Act establishing the Office of Coal Research, 30 U.S.C. 661-668.

This invention relates to improvements in the hydrogenation of coal tar and similar materials. More particularly, the invention pertains to the visbreaking of coal tar by hydrogenation in the presence of elemental iodine as the hydrogenation catalyst.

The production of gasoline and related distillate fuels from coal tar is well known and is described at length in the technical literature. In essence, the process consists in hydrogenating coal tar whereby it is converted into an oily liquid from which gasoline is recovered by fractional distillation.

In order to constitute a practical and economical source of gasoline, coal tar must be converted into a form suitable for processing in an oil refinery. As is well known, the modern refinery is designed primarily to operate with petroleum or crude oil; it cannot be operated using coal tar as raw material without extensive modification in design and construction. As a consequence coal tar requires further processing in order to adapt it as a refinery stock.

The method normally employed to convert coal tar into a suitable raw material capable of being used by the refinery is hydrogenation. This treatment transforms coal tar into a relatively mobile, oily fluid which can be easily handled and transported. Such liquefaction of coal tar by partial hydrogenation in commonly referred to as visbreaking. Aside from improving its physical form, hydrogenation upgrades the quality of the coal tar whereby it is substantially comparable to a high grade crude oil stock. The hydrogenation is particularly beneficial in that it frees the coal tar of oxygen, nitrogen and sulfur compounds which are undesirable and which may poison the hydrocracking catalysts used in the refinery. Moreover, the char solids normally present in coal tar can be readily removed from the liquefied material. A still further benefit derived from initial hydrogenation is that easily cracked cyclic hydrocarbons in the coal tar—notorious in causing fouling of catalyst bed—are transformed into more stable naphthenic systems.

Manifestly, preliminary hydrogenation or visbreaking is a necessary and essential adjunct in order to render coal tar suitable as a refinery stock material.

Although visbreaking converts coal tar into a usable refinery feed, the process is not entirely satisfactory as now practiced. For instance, the catalyst system—commonly a metal sulfide or molybdate suspended on metal grid—is subject to clogging by the suspended char particles contained in the coal tar. Catalyst poisoning is another serious and vexing problem. This results in the need for catalyst regeneration with consequent loss of time. Other problems of a lesser nature also plague the art.

It has now been discovered that the problems attendant the visbreaking of coal tar can be greatly diminished by conducting the process in the presence of a homogeneous catalyst system wherein the catalyst is elemental iodine or hydrogen iodide formed by reaction of hydrogen with iodine and the provision of such a process constitutes the principle object and purpose of the invention. Other ob-

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jects and purposes will become manifest subsequently.

In carrying out the process of the invention, generally excellent results are achieved by conducting the iodine catalyzed visbreaking at pressures from about 500 lb./sq. in. to about 5,000 lb./sq. in., preferably in the neighborhood of 1,000 to 3,000 lb./sq. in. The temperature is usually held to the range of 700° F. to 900° F., preferably of the order or 740° F. to 840° F. Although the amount of iodine catalyst is not critical, it should be used sparingly in the interest of good economics. In this connection we have ascertained that an iodine content of from about 0.2% to about 10.0% based on the coal tar provides a generous proportion of catalyst, while for practical purposes a range of from about 0.6% to about 1.0% is preferred.

It has also been discovered that elemental iodine retains its high catalytic efficiency even though the hydrogenating atmosphere contains relatively large amounts of other gases and this constitutes a further and unexpected advantage of the invention. In fact, we have ascertained that a hydrogen concentration as low as 25 mol percent does not significantly retard the catalytic action of iodine. As a consequence many waste and by-product gases which contain hydrogen can be used as a hydrogenation gas in the iodine-catalyzed visbreaking of coal tar. Normally, hydrogenation catalysts lose effectiveness when the hydrogen concentration falls below 70 mol percent; some even lose efficiency when the hydrogen content drops below 90 mol percent. By contrast a 50/50 mixture of hydrogen and diluent gas using iodine as the catalyst is as effective as 100% hydrogen when employing such typical catalysts as cobalt molybdate or nickel tungsten sulfide. At the present time we have not been able to account for this singular catalytic activity of elemental iodine. Possibly, the iodine and hydrogen exist in equilibrium with hydrogen iodide which may constitute the active catalyst.

The nature of the diluent gas is not critical. That is to say, mixing the hydrogen with such diverse gases as hydrogen sulfide, carbon monoxide, nitrogen, carbon dioxide and the like does not significantly effect the iodine-catalyzed hydrogenation. The only requirement is that the hydrogen not fall appreciably below the lower limit as above spelled out. We have found it particularly convenient and economical to practice the invention using reformer gas which is composed of hydrogen and carbon monoxide. It is produced by reacting coke with steam; the cost of the hydrogen in the mixture is about one-tenth that of an equivalent amount of pure hydrogen. The aforesaid mixture is effective even where the hydrogen constitutes only 25% of the hydrogenation gas. Moreover, iodine is not poisoned by sulfur, commonly present as hydrogen sulfide in reformer gas.

As a consequence it becomes possible to use waste gases such as steam-hydrocarbon reformer gases as the hydrogenating medium. The present invention thus makes available to the art the advantages and benefits attendant the use of iodine as a visbreaking catalyst while at the same time eliminating the usual economical drawbacks of this efficient albeit expensive catalytic agent.

It has been further ascertained that iodine is remarkably selective in its catalytic action as a visbreaking agent and this is another valuable aspect of the invention. Specifically, we have found that where coal tar is visbroken using iodine as the catalyst, the oxygen-containing compounds are reduced in preference to hydrogenation of the aromatic components. Since these oxygen-containing compounds are characterized by the presence of relatively polar ether linkages, their selective reduction by the iodine catalyst lowers the viscosity of the coal tar much more effectively than the catalytic agents now in use. Thus, in comparison tests, iodine hydrogenation of coal tar results in a ratio of aromatic hydrogen to total hydrogen of 1 to 4 thereby demonstrating only slight reduction

of aromatic ring systems. On the other hand, ammonium molybdate and copper chromite, typical prior art catalysts, exhibited ratios of 1:8.5 and 1:13, respectively, indicating a high degree of aromatic ring reduction. That is to say these catalysts did not display the unusual specificity for the oxygen compounds. Such preferentially catalytic activity of iodine taken together with its previously enumerated advantages make it eminently suitable as a visbreaking catalyst for converting coal tar into a high grade refinery stock material.

Although an independent and separate process, the invention can be operated in conjunction with a two-stage coal tar hydrogenation. In fact the two-stage operation is desirable in those instances where the coal tar refinery and the oil refinery are located in close proximity to one another. In this combined operation of the invention, which is illustrated by the block diagram in the attached drawing, a mixture of coal tar, hydrogen-containing gas, and iodine is introduced into a coal tar hydrogenator, and hydrogenation is carried out under reaction conditions as above defined. The resulting visbroken tar which is now a flowable, oily liquid is conveyed from the hydrogenator to a separator station where off gases are removed and aqueous waste liquors separated out and discarded. The oil is next piped to a hydrogenator where the second-stage hydrogenation is carried out with other catalysts, e.g., nickel tungsten sulfide, cobalt molybdate or the like. The second-stage hydrogenation removes residual nitrogen as ammonia, oxygen as water, sulfur as hydrogen sulfide and any iodine which may be present in the form of an organic iodide. The products from the oil hydrogenator are conducted to a receiver from which the contaminant free oil is removed. Off gases from the receiver and the visbreaker are led to a scrubber where carbon dioxide and iodine are removed. From the scrubber the off gas is led to an absorber station where high Btu and LP gases are taken off, while the purified hydrogen passes into the char stripper. The charge to the stripper is composed of bottoms from the visbreaker.

By operating in accordance with the aforesaid procedure, iodine is stripped from tar solids and off gas at both the visbreaker and hydrogenator units. By recovering iodine from the waste liquor the net iodine consumption is less than .5% based on the weight of the charge.

The invention is illustrated in greater detail by the following non-limiting example.

Example

One hundred grams of low temperature tar, obtained from the pyrolysis of a Wyoming subbituminous B coal in a fluidized bed, was charged to a 300 cc. autoclave along with 2.0 grams of sublimed iodine. The autoclave was pressurized to 3200 p.s.i. with a gas mixture consist-

ing of 50 mol percent hydrogen and 50 mol percent carbon monoxide, and was heated rapidly to 740° F. This temperature was maintained for three hours, during which time the maximum pressure in the bomb reached 4500 p.s.i. but dropped gradually to 4000 p.s.i. At the end of the heating period, the reactor was cooled, depressurized and emptied. The reactor products were filtered and 87 weight percent of oil, based on the dry, solids-free tar, were recovered along with 3.7 weight percent of solids including the catalyst. The viscosity of the oil was lowered from about 100,000 to less than 100 centipoises. The yield of hydrogenated oil was as high as that obtained when this same tar was hydrogenated with iodine or cobalt molybdate catalyst and 100% hydrogen.

As will be apparent to those skilled in the art numerous modifications and variations of the embodiments illustrated herein may be made without departing from the spirit of the invention or the scope of the appended claims.

What is claimed is:

1. A process for visbreaking coal tar comprising hydrogenating the coal tar at elevated pressures and temperatures in the presence of an iodine catalyst while using as the hydrogenating gas a mixture of hydrogen and diluent gas in a mol percent ratio of from about 25 mol percent:75 mol percent to about 75 mol percent:25 mol percent and recovering the visbroken coal tar.

2. The process of claim 1 wherein the diluent gas is carbon monoxide.

3. The process of claim 1 wherein the diluent gas is reformer gas.

4. The process of claim 1 wherein pressure is 1,000 to 3,000 lb./sq. in. of hydrogen.

5. The process of claim 1 wherein the temperature is 700° F. to 900° F.

6. The process of claim 1 wherein the hydrogenating gas is a mixture of hydrogen and carbon monoxide in a 50:50 mol percent ratio.

References Cited

UNITED STATES PATENTS

2,348,832	5/1944	Mauch	208—40
2,847,359	8/1958	Beuther et al.	208—40
2,850,436	9/1958	Beuther et al.	208—40
2,974,107	3/1961	Mertens	208—40

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,453,202

Dated July 1, 1969

Inventor(s) Louis D. Friedman and Ralph T. Eddinger

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

Column 3, line 44 ".5%" should read "0.05%" in the
patent.

SIGNED AND
SEALED

JAN 6 - 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents