

[54] **PROCESS FOR CONVERTING CELLULOSE**
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[57] **ABSTRACT**

A process for converting cellulose to a normally liquid oil, which includes contacting cellulose with water, a reducing gas and a catalytic compound containing a sulfur component and an alkali metal or ammonium ion component at particular conditions of temperature and pressure to insure a liquid water phase at conversion conditions employed. The reducing gas may be carbon monoxide, hydrogen, or a mixture thereof.

8 Claims, No Drawings

PROCESS FOR CONVERTING CELLULOSE

BACKGROUND OF INVENTION

This invention relates to a process for converting cellulose to a hydrocarbonaceous, normally liquid oil.

This invention also relates to a process for converting municipal waste materials into valuable hydrocarbonaceous compounds.

It is known that cellulose can be converted into a hydrocarbonaceous tar by treatment with water and carbon monoxide at elevated temperatures and pressures. The conversion of cellulose to a hydrocarbonaceous liquid is advantageous in two aspects in particular. First, this type of conversion provides a method for reducing the volume of the enormous amount of municipal refuse which is normally buried or burned in order to effect disposal. Further, burning and/or burying refuse is wasteful of the hydrocarbonaceous material, primarily in the form of cellulose, which are present in such refuse. By converting the cellulose components of typical municipal waste matter into valuable liquid hydrocarbonaceous products, the volume of the refuse can be diminished by as much as 90%. The hydrocarbonaceous liquid products recovered may be employed as fuel or as feed stocks in processes for producing chemical derivatives. Previously disclosed methods for converting cellulose using water and a reducing gas are able to achieve only undesirably low rates of conversion. Prior art methods are hampered in that hydrogen has been found inactive when used as the reducing gas in place of carbon monoxide, whereas carbon monoxide is an expensive reducing gas relative to a carbon monoxide-hydrogen mixture such as synthesis gas.

SUMMARY OF INVENTION

An object of the present invention is to provide a process for converting cellulose to normally liquid hydrocarbonaceous material. Another object of the present invention is to provide a process for reducing the volume of cellulose-containing municipal refuse. A further object of the present invention is to provide a process for converting cellulose to a hydrocarbonaceous liquid utilizing a compound containing a sulfur component and an alkali metal or ammonium ion component as a catalyst.

Another object of the present invention is to provide a process for converting cellulose to a hydrocarbonaceous liquid, utilizing hydrogen or a mixture thereof with carbon monoxide as a reducing gas, which provides a conversion equally as good as the conversion obtained utilizing carbon monoxide alone as the reducing gas in the conversion operation.

In an embodiment, the present invention relates to a process for converting cellulose to a normally liquid hydrocarbonaceous product which comprises contacting the cellulose with water, a reducing gas, and a catalytic compound containing a sulfur component and an alkali metal or ammonium ion component, at conversion conditions including a temperature of about 200°C. to about 375°C. and a pressure sufficient to maintain at least a portion of the water as a liquid phase, and recovering the hydrocarbonaceous product from the resulting mixture.

By employing a compound containing a sulfur component and an alkali metal or ammonium ion component in combination with water and a reducing gas, and by utilizing temperatures and pressures in the conver-

sion operation whereby the water is maintained at least partially as a liquid, cellulose may be converted into liquid hydrocarbonaceous oil in high yields. Using the process of the present invention, hydrogen may be substituted as the reducing gas in place of carbon monoxide, so that a mixture of carbon monoxide and hydrogen, such as synthesis gas, can be economically employed in the present process.

DETAILED DESCRIPTION OF INVENTION

Any cellulose-containing material may be employed as the feed stock in the present process. For example, paper, cardboard, wood and other conventional vegetable matter which is normally found in municipal refuse may be employed. It is contemplated that the present process may be performed using a mixture of cellulose-containing materials with refractory materials such as metals, plastics, etc., whereby the cellulose can be liquefied and easily separated from the refractory solid materials by decantation. The refractory materials may then be discarded or disposed of in any conventional manner.

The applicable sulfur-containing and alkali metal ion-containing or ammonium ion-containing catalytic compounds, include particularly sulfides and sulfur-containing compounds capable of being catalytically reduced at the liquefaction conditions hereinafter described. The applicable compounds include, for example, alkali metal sulfides, alkali metal sulfites, alkali metal thiosulfates, ammonium sulfide, ammonium sulfite, ammonium thiosulfate, etc. Particular compounds which are preferred for use as the sulfur-containing catalytic compound in the present process include sodium sulfide, potassium sulfide, sodium sulfite, potassium sulfite, sodium thiosulfate, potassium thiosulfate, sodium hydrosulfide, potassium hydrosulfide, sodium hydrogen sulfite, potassium hydrogen sulfite, sodium pyrosulfite, potassium pyrosulfite, the disulfides, trisulfides, tetrasulfides, and pentasulfides of sodium and potassium. Also preferred are the analogous ammonium compounds including ammonium sulfide, ammonium hydrosulfide, ammonium sulfite, ammonium hydrogen sulfite and ammonium thiosulfate. Other suitable compounds include lithium sulfide, lithium hydrosulfide, lithium sulfite, rubidium sulfides, cesium sulfides, etc.; however, sodium and potassium are particularly preferred alkali metals. Other sulfur-containing and alkali metal ion- or ammonium ion-containing compounds may be employed but not necessarily with equivalent results. Oxysulfur compounds are particularly preferred in the present process.

The reducing gas employed in the present process may be pure hydrogen or pure carbon monoxide. A mixture of these gases is also suitable. The reducing gas may be commingled with one or more gases or vapors which are relatively inert in the conversion operation, including nitrogen, carbon dioxide, etc. One convenient, suitable source of the reducing gas is a synthesis gas produced by reaction of carbon or hydrocarbons with steam to produce carbon monoxide and hydrogen. A variety of methods for producing a synthesis gas suitable for use in the present process are well known in the art.

Conversion conditions, in the present process, include a temperature of about 200°C. to about 375°C. and a pressure at least sufficient to provide a liquid water phase at the desired temperature. For example,

in an operation wherein it is desired to maintain a temperature of about 200°C., a pressure of at least about 20 atmospheres is maintained at conversion conditions. In high temperature operations, e.g., 350°-375°C., a pressure of about 135 atmospheres to about 220 atmospheres or more is maintained. In the temperature range between about 200°C. and about 300°C., the primary utility of the process of the present invention is in the reduction of the volume of municipal refuse. At this temperature range, the oil produced from cellulose is heavy and approximately of the same consistency as a crude oil. At higher temperature operations, between about 300°C. and about 375°C., the oil produced is lighter and may be used directly as a feed stock to provide petrochemicals, etc., without the necessity of further processing, as may be necessary in order to utilize the oil obtained at lower temperature operation.

The amount of water employed in the present process in contact with the cellulose at conversion conditions is between about 10 wt.% and about 1,000 wt.% based on the amount of cellulose to be converted. Good results are obtained when the amount of water is between about 50 wt.% and about 200 wt.% of the cellulose. The amount of the sulfur-containing catalytic compound utilized in contact with the cellulose is sufficient to provide a concentration of about 10 wt.% to about 100 wt.% based on the cellulose. A concentration of about 25 wt.% to about 75 wt.% is particularly preferred. The sulfur-containing compound may conveniently be employed as an aqueous solution of, for example, sodium thiosulfate or ammonium thiosulfate in the water employed. When this method is utilized, it is preferred to maintain a concentration of about 10 wt.% or more of the sulfur-containing compound in solution in the water. The superatmospheric pressures employed at conversion conditions in the present process may be wholly supplied by the reducing gas, or may be supplied, in part, by inert gases, water vapor, etc. In any case, the partial pressure of the reducing gas is maintained at least about 10% of the total pressure. The amount of the reducing gas employed is generally about 0.5 standard cubic feet (SCF) to about 175 SCF per pound of cellulose in the matter to be processed. Preferably the amount of the reducing gas utilized is about 20 SCF to about 75 SCF per pound of cellulose.

The process of the present invention may be performed in a batch-type operation or a continuous-type operation. When a batch-type operation is utilized, fixed amounts of the cellulose-containing material, water, the sulfur-containing catalytic compound and the reducing gas are charged to a suitable reactor such as an autoclave. The reactants are contacted in the reactor for a period of time sufficient to produce the conversion of the cellulose to the normally liquid oil and then the mixture in the reactor is withdrawn and the desired liquid hydrocarbonaceous products are separated from the any remaining solids and water and recovered. A suitable contact time in a batch-type operation is about 30 minutes to about 300 minutes, preferably about 60 minutes to about 200 minutes. In a continuous operation, the cellulose-containing material, water, the sulfur-containing compound and the reducing gas are continuously charged to a suitable reactor capable of internal agitation and contacted therein. The mixture of the hydrocarbonaceous product, water, reducing gas and any remaining solids, is continuously withdrawn from the reactor and the desired hydrocarbo-

naceous product is separated and recovered. A suitable liquid hourly space velocity in a continuous-type operation (volume of the reactor divided by the total volume of cellulose-containing materials, water, and reducing gas charged per hour) of about 0.1 to about 1 may be employed, and a liquid hourly space velocity of about 0.25 to about 0.5 is particularly preferred. The reactor utilized in the present process may be any suitable vessel which can maintain the cellulose-containing materials, water and reducing gas at the desired temperature and pressure in order to provide sufficient conversion. For example, a conventional rocking autoclave is a suitable reactor for use in a batch-type operation. A variety of suitable vessels for use as the reactor are known in the art. Preferably, the reactor includes some means for admixing the cellulose-containing materials with the water and reducing gas by stirring or other agitation.

The mixture recovered after the conversion operation, in addition to the desired liquid hydrocarbonaceous product will also contain water, which will generally be in a separate phase from the hydrocarbonaceous product. Thus, the hydrocarbonaceous product may conveniently be separated from the water and from any remaining solid materials such as metals, plastics, etc., by simple mechanical separation of the solids and the water. The water phase thus recovered may be recirculated to the liquefaction step for further use. Similarly, any reducing gas which is not consumed during the conversion operation may be recovered and recirculated to the reactor. The water phase recovered from the operation contains some water-soluble organic materials and may also contain unconsumed sulfur-containing compound. The water may be evaporated leaving behind an organic material which is useful as an agricultural fertilizer.

The following illustrative embodiments are presented in order to demonstrate particular applications of the process of the present invention. The illustrations are presented for the purpose of exemplification and contrast with prior art only, and are not intended as limitations on the generally broad scope of the invention. Those skilled in the art will recognize from the foregoing and from the illustrations hereinafter presented that many variations and embodiments within the scope of the present invention are apparent.

ILLUSTRATIVE EMBODIMENT I

In order to illustrate the process of the present invention, the conversion of commercially available paper towels to a liquid hydrocarbonaceous oil is undertaken. One hundred grams of commercial paper towel is placed on 850 cc. rocking autoclave. 275 cc. of water and 30 grams of $(\text{NH}_4)_2\text{S}_2\text{O}_3$ are also placed in the autoclave. The autoclave is sealed and sufficient carbon monoxide is charged to provide 70 atmospheres carbon monoxide pressure in the autoclave. The contents of the autoclave are then heated to a temperature of 300°C. and agitated at this temperature for 4 hours. The autoclave is then cooled to room temperature and excess pressure is released. The liquid contents of the autoclave are removed and are observed to comprise a water phase and an oil phase. The oil phase is decanted to separate it from the water phase and is recovered as the product of the operation. The oil phase is analyzed and found to contain 75 wt.% carbon and 9 wt.% hydrogen.

ILLUSTRATIVE EMBODIMENT II

One hundred grams of commercial paper towels is placed in the 850 cc. autoclave with 200 grams of water and 30 grams of $\text{Na}_2\text{S}_2\text{O}_3$. The autoclave is sealed and sufficient hydrogen is charged to provide 70 atmospheres hydrogen pressure. The contents of the autoclave are then heated to 300°C . and agitated at that temperature for 4 hours. The autoclave is then cooled to room temperature and excess pressure is released. The liquid contents of the autoclave are then removed, and the hydrocarbonaceous oil product is separated from water by decantation and recovered. In order to demonstrate the advantages of the present process, the same procedure is followed using NaHCO_3 , known to prior art as a catalyst effective with carbon monoxide and water. One hundred grams of paper towel, 200 grams of water and 30 grams of NaHCO_3 are placed in the 850 cc. autoclave. The autoclave is sealed and sufficient hydrogen is charged to provide 70 atmospheres hydrogen pressure. The contents of the autoclave are then heated to 300°C . and agitated for 4 hours. The autoclave is then cooled to room temperature and excess pressure is released. When the liquid contents of the autoclave are removed and examined, no oil phase is observed to be present, indicating complete lack of conversion of the towel to a hydrocarbonaceous liquid. Thus, NaHCO_3 is not a catalyst when using hydrogen as the reducing gas.

ILLUSTRATIVE EMBODIMENT III

One hundred grams of commercial paper towel, 200 grams of water and 30 grams of Na_2S are placed in the 850 cc. autoclave. The autoclave is sealed and sufficient carbon monoxide is introduced to provide 35 atmospheres carbon monoxide pressure. Sufficient hydrogen is then charged to provide a hydrogen pressure of 35 atmospheres and a total pressure of 70 atmospheres. The contents of the autoclave are heated to 300°C . and agitated for 4 hours. The autoclave is then cooled to room temperature and excess pressure is released. The liquid contents of the autoclave are removed and observed to comprise an oil phase and a water phase. The oil phase is separated by decantation and recovered as the hydrocarbonaceous product of the operation.

ILLUSTRATIVE EMBODIMENT IV

One hundred grams of commercial paper towel, 200 grams of water and 30 grams of NaHSO_3 are placed in the 850 cc. autoclave. The autoclave is sealed and sufficient carbon monoxide and hydrogen are introduced to provide 35 atmospheres partial pressure for each gas and a total pressure of 70 atmospheres. The contents of the autoclave are heated to 300°C . and agitated at

that temperature for 4 hours. The autoclave is then cooled to room temperature and excess pressure is released. The liquid contents of the autoclave are removed and are observed to comprise a water phase and an oil phase. The oil phase is separated by decantation and recovered as the product of the process.

As shown by the foregoing description and illustrations, the process of the present invention provides a novel and superior method for converting cellulose into a liquid hydrocarbonaceous oil which may be employed as a fuel or as a feed stock to provide valuable chemical derivatives. It is also apparent that the present invention provides a particularly useful method for converting cellulose in that hydrogen gas may be employed in place of, or in combination with, carbon monoxide as the reducing gas in the present process. This is in contrast to prior art processes utilizing water and a reducing gas in which only carbon monoxide has been found to be effective as a reducing gas. Further, it is clear that the present invention provides a valuable method for radically reducing the volume of municipal refuse by converting the cellulose-containing components of such refuse to a valuable hydrocarbonaceous product which can easily be separated from solid, unconverted components of the refuse and can be used as a fuel or further converted, while the unconverted refuse is substantially reduced in volume, facilitating disposal.

I claim as my invention:

1. A process for converting cellulose to a normally liquid hydrocarbonaceous product which comprises contacting paper with water, a reducing gas a catalytic compound selected from the group consisting of alkali metal and ammonium sulfides, sulfites and thiosulfates at conversion conditions including a temperature of about 200°C . to about 375°C . and a pressure sufficient to maintain at least a portion of the water as a liquid phase, and recovering the hydrocarbonaceous product from the resulting mixture.
2. A process according to claim 1 wherein said reducing gas comprises hydrogen.
3. A process according to claim 1 wherein said reducing gas comprises carbon monoxide.
4. A process according to claim 1 wherein said catalytic compound is an alkali metal sulfide.
5. A process according to claim 1 wherein said catalytic compound is an alkali metal sulfite.
6. A process according to claim 1 wherein said catalytic compound is an alkali metal thiosulfate.
7. A process according to claim 1 wherein said alkali metal is selected from sodium and potassium.
8. A process according to claim 1 wherein said catalytic compound is selected from ammonium sulfide, ammonium sulfite and ammonium thiosulfate.

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