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PREPARATION OF UNSATURATED HYDROCARBONS FROM OXYGEN-CONTAINING ORGANIC MATERIALS

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This invention relates to the preparation of unsaturated hydrocarbons from oxygen-containing organic materials. It pertains particularly to the preparation of low molecular weight, unsaturated hydrocarbons such as acetylene and ethylene.

While it is well known to prepare acetylene, ethylene and other low molecular weight, unsaturated hydrocarbons by various thermal processes from carbonaceous and hydrocarbonaceous raw materials such as coal and petroleum, it heretofore has not been known to prepare such products on a commercial scale from oxygen-containing starting materials such as lignin, lignocellulose and the carbohydrates. Indeed, in view of the high degree of reactivity of elemental oxygen at elevated temperatures, it has been considered impossible to use such starting materials for the indicated purpose in view of the likelihood of forming oxygen-containing end products.

The desirability is readily apparent of providing a commercial process for the large scale production of highly useful industrial chemicals such as acetylene and ethylene from a replenishable source such as wood and from waste products such as bark and pulp mill spent liquors.

Accordingly, it is the general object of the present invention to provide a commercial process for the production of unsaturated hydrocarbons such as acetylene and ethylene from raw materials containing a high percentage of oxygen, such as lignin, lignocellulose, and the carbohydrates.

A further important object of the invention is the provision of a process for making unsaturated hydrocarbons from pulp mill spent liquors, which process may be operated as an adjunct of paper mill pulping procedures, without abnormal loss of pulping chemicals, and without destroying the delicate chemical balance which must be preserved during the pulping process.

We now have discovered that, unexpectedly and contrary to the teachings of the prior art, unsaturated hydrocarbons such as acetylene and ethylene may be obtained in yields of up to 50% of the theoretical by a process which, broadly considered, comprises reducing the material to finely divided form, heating it rapidly in a substantially inert gaseous environment to a selected temperature of at least 1000° F., maintaining it at the selected temperature until a substantial proportion of it has been converted to a reaction product including the desired unsaturated hydrocarbons, rapidly cooling the reaction product, and separating the unsaturated hydrocarbon components from it.

As an important modification of the foregoing procedure, it may be carried out as an adjunct of paper mill pulping procedures. In this case the process comprises cooking lignocellulose in an aqueous medium with a predetermined proportion of an inorganic lignocellulose pulping agent for substantial separation of the lignin from the cellulose, separating the resulting cellulosic pulp from the residual spent liquor, separating the inorganic salt content of the liquor and returning it to the pulping of a further quantity of the lignocellulose, separating the lignin content of the liquor as a finely divided solid, and then pyrolyzing the solid in a substantially inert gaseous en-

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vironment as set forth above. In this way the unsaturated hydrocarbon products may be manufactured without abnormal loss of pulping chemicals and without destroying the material balance in the digesters.

As raw materials for the process of our invention, there may be employed a diversity of oxygen-containing substances. Thus the alkali lignins, including soda lignin and kraft lignin, are eminently suitable for the present purpose. These preferably are treated first for removal of their inorganic salt content, which then may be cycled to the chemical recovery system of the pulp mill.

In addition, the sulfonated lignins contained in sulfite spent liquor may be employed, keeping in mind that the sulfur contained in such liquor may serve as a hydrogen scavenger during the pyrolysis reaction, thus reducing correspondingly the yield of unsaturated hydrocarbon products. Hence if use of lignins of this class is contemplated, their desulfonation by reaction with lime, or otherwise, is recommended as a preliminary treatment.

Whatever their source, the pulping spent liquors are evaporated or chemically treated for separation of the solid lignins. These then are dried sufficiently to convert them to a finely divided powder which may be handled easily.

The lignocellulose materials such as the woods and barks of various tree species, and various non-woody plant materials such as bagasse, straw and cornstalks, are also applicable broadly to the purposes of the present invention. When using these materials they first are dried, if desired, and reduced to finely divided form in any suitable grinding or comminuting apparatus. Although the degree of subdivision is variable, depending upon the nature of the materials and the reaction conditions, in general it is preferred to reduce them to a particle size of not over 20 mesh, U.S. Sieve Series.

The various carbohydrates, such as sugars, starch and, particularly, cellulose, also are applicable as starting materials for the presently described process. In this case also the materials first are reduced to a dry powder, preferably one having a particle size of not over 20 mesh, U.S. Sieve Series.

The selected starting material is introduced into a reaction zone containing a substantially inert, or at least non-detrimental, gas such as helium, carbon monoxide, argon, or neon. Nitrogen also may be employed, although in this case hydrogen cyanide may be formed as a by-product. Preferably the solid material is introduced into the reaction zone by entraining it in a stream of the selected gaseous carrier.

The reaction zone may be heated to the desired level and in any suitable manner, as by partial combustion of the reacting material, indirect combustion, electrical resistance heating, electric arc heating, etc.

It is critical to the success of the presently described process that the temperature of the material be elevated rapidly in the reaction zone to a level of at least 1000° F. If this is not done, the usual oxygen-containing pyrolysis products of lignin and woody materials are obtained. These include tars, resins, pyrolygneous acids and the like.

However, when the temperature is elevated rapidly to the indicated level, there is produced a reactive mixture of carbon and hydrogen atoms, radicals and ions which will interact with each other to produce ethylene or acetylene as principal products depending primarily upon the reaction temperature. Thus temperatures of between 1000° F. and about 2200° F. favor the production of ethylene. At temperatures of from about 2200° F. to 3500° F. substantial amounts of acetylene are formed.

These two desired end products, however, have a marked tendency to decompose at the reaction temperature into carbon and hydrogen. Thus it becomes crit-

ically essential to carry out the reaction as a flash reaction, or at least to restrict severely the dwell time of the reactants in the reaction zone to a period of from 10^{-4} seconds to one of no more than 10 seconds. When producing acetylene, the preferred dwell time is from 10^{-4} second to 0.5 second. When producing ethylene it is from 10^{-2} second to 2 seconds. In both cases the reaction period will vary inversely with the reaction temperature.

At the conclusion of the reaction period the reaction mixture is cooled rapidly, preferably by quenching it in a spray of water or other liquid, or by passing it through a heat exchanger cooled efficiently by water or other cooling medium.

After cooling, the gaseous components of the reaction mixture are separated from any suspended carbon which may have been formed. The acetylene and ethylene products are recovered and separated from each other by any of the methods conventionally employed for this purpose.

The process of the invention is illustrated by the following examples, wherein the yields are expressed as yields by weight, based on the weight of the oxygen-containing starting material.

Example 1

A 4-way T reactor was fitted with two tungsten wires connected to a high voltage source. An arc was struck between the wires. Dry powdered kraft lignin obtained by the acidification of kraft black liquor was blown through the arc using helium as a carrier gas. The maximum temperature of the arc was about 3600° F. An analysis of the gaseous product indicated an acetylene yield of 14%.

The foregoing procedure was repeated, using the following as starting materials, and with the indicated yields of acetylene: (a) lime-desulfonated calcium-base sulfite spent liquor, 12.5%; (b) finely powdered Douglas fir wood, 13%; and (c) powdered alpha-cellulose, 14.5%.

Example 2

This example illustrates the application of resistance heating to the presently described process.

In a 4-way T tube reactor was placed a coil wound with $\frac{3}{16}$ " diameter No. 28 tungsten wire. The coil was connected to copper wire sealed into the system and a current of 500 watts passed through the coil, the temperature of which reached a level of from 3500–4500° F.

Precipitated kraft lignin was blown onto the coil using helium as a gaseous carrier. The gases were removed from the reaction zone immediately and collected over saturated brine. An acetylene yield of 23% was obtained.

Example 3

A furnace consisting of a 1" ceramic tube surrounded by a $\frac{1}{4}$ " layer of flake graphite held in place by an alumina cylinder was heated with Rf current. The heating zone was 5" long and was packed loosely for about one-half its distance with broken ceramic. Water cooled copper tubes communicated with the ceramic tube at its upstream and downstream ends. Means were provided for admitting the powdered feed in an inert carrier gas at a controlled flow rate, thereby enabling various residence times in the furnace.

With the temperature at 2900° F. and a helium flow rate of 2700 ml./min., 2.6 grams of dry precipitated kraft lignin were added to the furnace in 30 seconds. The gaseous product was collected over water. Analysis indicated an acetylene yield of 8.6% and an ethylene yield of 2.5%.

Example 4

The procedure of Example 3 was repeated, heating the furnace to 2100° F. 2.6 grams of dry, precipitated kraft lignin were added in 30 seconds with a helium flow rate

of 2700 ml./min. In this case a 3.5% yield of acetylene and a 7.2% yield of ethylene were obtained.

Example 5

The procedure of Example 3 again was repeated, with the furnace heated to 2600° F. and the helium flow rate adjusted to 2700 ml./min. Under these conditions, 1.8 grams of powdered Douglas fir wood were passed through the system in about 2 minutes. An acetylene yield of 13% and an ethylene yield of 4.6% were obtained. Bubbling the gaseous product through silver nitrate test solution resulted in the formation of a characteristic precipitate of solid silver carbide-silver nitrate.

Example 6

Into the furnace of Example 3 heated to 2700° F. using a helium flow of 4000 ml./min. were passed 2 grams of 60-mesh whole bagasse in about 3 minutes. An acetylene yield of 15% was obtained.

Example 7

Using the furnace and conditions of Example 3, 2 grams of 60-mesh Douglas fir bark was passed through the furnace. A yield of 12.5% acetylene was obtained.

Example 8

A plasma was made by passing argon through a 1" quartz tube surrounded by a 17-turn water-cooled $\frac{3}{16}$ " copper tubing coil connected to a radio frequency generator. The temperature of the plasma was from 4000° F. to 5000° F. Careful addition of 0.3 gram powdered bagasse into the plasma in about 3 minutes resulted in collection of a 17% yield of acetylene. There was no evidence of the formation of any ethylene or methane.

Thus it is apparent that by the present invention we have provided a process for making unsaturated hydrocarbons such as ethylene and acetylene from oxygen-containing raw materials such as lignin, lignocellulose and the carbohydrates. The process is applicable on a large commercial scale and makes useful various categories of materials, notably pulping spent liquors, sawdust and bark, which are available in very large quantities and normally present a disposal problem. In addition, the process may be included in normal pulp mill recovery procedures without disturbing material balances or causing abnormal loss of pulping chemicals.

Having thus described our invention in preferred embodiments, we claim as new and desire to protect by Letters Patent:

1. The process of preparing unsaturated hydrocarbons of the group consisting of acetylene and ethylene from oxygen-containing organic materials comprising at least one member of the class consisting of the lignins, the lignocelluloses, and the carbohydrates, said process comprising: reducing the material to a finely divided form, rapidly heating the material in a substantially inert gaseous environment to a selected temperature of at least 1000° F., maintaining the material at the selected temperature for a time of from 10^{-4} seconds to about 10 seconds, thereby converting a substantial proportion of it to a reaction product including a substantial proportion of unsaturated hydrocarbon, rapidly cooling the reaction product, and separating the unsaturated hydrocarbon component therefrom.

2. The process of claim 1 wherein the oxygen-containing organic material comprises a lignin.

3. The process of claim 1 wherein the oxygen-containing organic material comprises a lignin-containing pulping spent liquor.

4. The process of claim 1 wherein the oxygen-containing organic material comprises soda lignin.

5. The process of claim 1 wherein the oxygen-containing organic material comprises kraft lignin.

6. The process of claim 1 wherein the oxygen-containing organic material comprises lignocellulose.

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7. The process of claim 1 wherein the oxygen-containing organic material comprises the wood of trees.

8. The process of claim 1 wherein the oxygen-containing organic material comprises the bark of trees.

9. The process of claim 1 wherein the oxygen-containing organic material comprises non-woody plants.

10. The process of claim 1 wherein the oxygen-containing organic material comprises bagasse.

11. The process of claim 1 wherein the oxygen-containing organic material comprises a carbohydrate.

12. The process of claim 1 wherein the oxygen-containing organic material comprises cellulose.

13. The process of claim 1 wherein the material is heated to a temperature of from 1000-2200° F. and wherein the principal unsaturated hydrocarbon product comprises ethylene.

14. The process of claim 1 wherein the material is heated to a temperature of from 2200-3500° F. and wherein the principal unsaturated hydrocarbon product comprises acetylene.

15. The process of claim 1 wherein the reaction product is cooled rapidly by quenching it in water.

16. The process of making unsaturated hydrocarbons of the groups consisting of acetylene and ethylene which comprises cooking lignocellulose in an aqueous medium with a predetermined proportion of an inorganic lignocellulose pulping agent for substantial separation of the lignin from the cellulose, separating the resulting cellulosic pulp from the residual spent liquor, separating the inorganic compound content of the liquor and returning it to the pulping of a further quantity of lignocellulose, separating the lignin content of the liquor as a finely divided solid, rapidly heating the solid lignin in a substantially inert gaseous environment to a selected temperature of at least 1000° F., maintaining the lignin

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solids at the selected temperature for a time of from 10⁻⁴ seconds to about 10 seconds, thereby converting a substantial proportion thereof to a reaction product including the unsaturated hydrocarbon, rapidly cooling the reaction product, and separating the unsaturated hydrocarbon therefrom.

17. The process of claim 16 wherein the inorganic lignocellulose pulping agent comprises a kraft pulping agent.

18. The process of claim 16 wherein the inorganic lignocellulose pulping agent comprises a soda pulping agent.

19. The process of claim 16 wherein the inorganic lignocellulose pulping agent comprises a sulfite pulping agent.

20. The process of claim 16 wherein the inorganic lignocellulose pulping agent comprises a sulfite pulping agent and including the step of desulfonating the spent liquor preliminary to separating the lignin solids.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 5,283	Elmer	Feb. 23, 1869
25,316	Breisach	Sept. 6, 1859
87,156	Elmer	Feb. 23, 1869
2,126,150	Stryker	Aug. 9, 1938
2,165,820	Smyers	July 11, 1939

FOREIGN PATENTS

455,567	Great Britain	Oct. 23, 1936
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OTHER REFERENCES

Dolique et al.: "Chemical Abstracts" (1955), volume 49, No. 21, page 14912f.