

1

3,796,650

COAL LIQUEFACTION PROCESS

Peter Urban, Northbrook, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill.

No Drawing. Filed July 24, 1972, Ser. No. 274,145

Int. Cl. C10g 1/00, 1/06

U.S. Cl. 208—10

5 Claims

ABSTRACT OF THE DISCLOSURE

A process is disclosed for de-ashing and liquefying coal which comprises contacting comminuted coal with water, at least a portion of which is in the liquid phase, a reducing gas and a compound selected from ammonia and carbonates and hydroxides of alkali metals, at liquefaction conditions, including a temperature of 200–370° C. to provide a hydrocarbonaceous product.

BACKGROUND

This invention relates to a process for converting carbonaceous solids to more valuable hydrocarbonaceous products. More specifically, this invention relates to a process for de-ashing and converting coal to hydrocarbon products by contacting the coal with liquid water, a compound selected from ammonia and hydroxides and carbonates of alkali metals, and a reducing gas at particular liquefaction conditions to provide the hydrocarbon products.

Several methods for converting coal to more valuable liquid or liquefiable products are known to the art. One method employs destructive distillation of the coal. More recently, high pressure hydrogenation and solvent extraction techniques have been employed. One of the more onerous difficulties encountered in prior coal liquefaction art is the separation of the liquefied hydrocarbonaceous products from the unconverted coal, ash, and various solid inorganic materials invariably contained in the raw coal. Under typical prior art liquefaction conditions, the solids are dispersed in the liquefied material and in the organic solvent, if one is used, in a finely divided particulate state, rendering separation extremely difficult. Settling, centrifuging and filtration techniques have been employed with some success, but are economically unattractive as a means for de-ashing the liquefied materials.

The product of coal liquefaction typically requires further treatment by techniques analogous to petroleum refining methods in order to convert the liquefaction product into valuable liquid hydrocarbons such as gasoline, or to provide benzene and other organic chemicals. This further treatment generally comprises catalytic hydrogenation and cracking of the hydrocarbonaceous tars that result from liquefaction. It has been found that, in general, the particulate matter must be removed from the liquefaction product before such further treatment can effectively and economically be undertaken. Consequently, the prior art has concentrated on methods for economically separating ash from the liquefaction product. The process of this invention at least partially obviates the need for such separation techniques, by reducing the ash content of the liquefaction product to such a low level that further catalytic treatment of the liquefaction product can be undertaken directly without further separation of solids.

Another major drawback of prior art coal liquefaction methods has been the requirement for large amounts of hydrogen both in high pressure hydrogenation and in solvent extraction. It has been suggested that this problem can be overcome by converting only that small fraction of the coal which is relatively rich in hydrogen. It is obviously more desirable to convert as large a fraction as possible of the coal to valuable products. A process which

2

could employ a low cost substitute for hydrogen or substantially reduce the amount of hydrogen needed would be economically more attractive than prior art methods and would constitute a significant advancement.

SUMMARY

An object of the present invention is to provide a novel process for the liquefaction of carbonaceous solids to produce more valuable hydrocarbonaceous products.

A further object of the present invention is to provide an improved process for liquefying coal, utilizing liquid phase water and a readily available reducing gas, to produce valuable hydrocarbonaceous products.

A particular object of the present invention is to provide a process for liquefying coal in which the ash content of the product is reduced, resulting in a hydrocarbonaceous product of greater utility.

In an embodiment, the present invention relates to a process for converting a solid carbonaceous material to a hydrocarbonaceous liquefaction product which comprises the steps of: (a) contacting said solid material with a reducing gas, with water, at least a portion of which is liquid, and with a catalytic compound selected from ammonia, alkali metal hydroxides and alkali metal carbonates, at liquefaction conditions including a temperature of about 200° C. to about 370° C. and a pressure sufficient to maintain said water at least partially in the liquid phase; and (b) recovering said hydrocarbonaceous product from the resulting mixture.

In a more limited embodiment, the present invention relates to a process for converting a solid carbonaceous material to a hydrocarbonaceous liquefaction product which comprises the steps of: (a) contacting said solid material with a reducing gas, with water, at least a portion of which is liquid, and with a catalytic compound selected from ammonia, alkali metal hydroxides and alkali metal carbonates, at liquefaction conditions including a temperature of about 200° C. to about 370° C. and a pressure sufficient to maintain said water at least partially in the liquid phase; (b) separating the resulting mixture into an aqueous phase and a hydrocarbonaceous phase; and (c) recovering said liquefaction product from said hydrocarbonaceous phase.

I have discovered that coal and other carbonaceous solid materials can be liquefied to produce valuable hydrocarbonaceous products by treating the coal with a relatively large quantity of water which is at least partially in the liquid phase, and with a reducing gas and a compound selected from ammonia and hydroxides and carbonates of alkali metals. I have found that the ash content of the coal can thereby be reduced significantly and that the hydrocarbonaceous product can be further processed catalytically, in a manner analogous to petroleum refining methods, without the necessity of removing ash and undissolved carbonaceous materials. In place of the hydrogen employed in prior art, coal liquefaction methods, carbon monoxide, or a mixture of carbon monoxide with hydrogen, provides an effective reducing gas in the present process, permitting the use of low cost sources of reducing gas, e.g. synthesis gas.

PREFERRED EMBODIMENT

The carbonaceous solid materials which can be utilized in the present process to provide the hydrocarbonaceous product include any sort of coal, lignite, peat, oil shale, tar sand or similar substance. The preferred carbonaceous solid is a bituminous coal. For example, an Illinois Bellville District stoker coal having a moisture and ash free volatile content of greater than about 20% or higher is suitable. Although not essential to the process, it is preferred that the carbonaceous solid to be employed in the process is first reduced to a particulate, comminuted form. Preferably, the

carbonaceous solid is ground or pulverized to provide particles sufficiently small to pass through a 100 mesh Tyler sieve or smaller. Coal ground sufficiently to pass through a 200 mesh sieve is particularly preferred.

The alkali metal compounds which can be employed in the present process include sodium hydroxide, potassium hydroxide, sodium carbonate, sodium hydrogen carbonate, potassium carbonate, potassium hydrogen carbonate, potassium sodium carbonate, or a mixture of two or more of the above. Similar salts of other alkali metals such as lithium or rubidium can also be employed, but not necessarily with equivalent results. The above noted sodium salts are preferred, particularly sodium carbonate and sodium hydrogen carbonate.

Ammonia can be employed in place of the foregoing alkali metal compounds. Nitrogen-containing organic compounds can also be utilized to provide ammonia by decomposition. Suitable organic compounds include hexamethylene tetramine, formamide, ammonium acetate, guanidine, biuret, and ammonium salts of phenolic acids such as phenol, resorcinol, etc.

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 liquefaction reaction, 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 known in the art.

Liquefaction conditions, in the present process, include a temperature of about 200° C. to about 370° 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 higher temperature operations, e.g., 350–370° C., a pressure of about 135 atmospheres to about 220 atmospheres or more is maintained. Best results are achieved when a temperature of about 250° C. to about 350° C. is employed. It is also preferred to employ pressures below about 400 atmospheres.

The amount of water contacted with the carbonaceous solid at liquefaction conditions is between about 100 wt. percent and about 1000 wt. percent of the carbonaceous solid. Good results are obtained when the amount of water is between about 100 wt. percent and about 300 wt. percent of the carbonaceous solid. The amount of ammonia or alkali metal compound contacted with the solid is sufficient to provide a concentration of about 0.1 wt. percent to about 1000 wt. percent. A concentration of about 0.1 wt. percent to about 200 wt. percent, based on the carbonaceous solid, is preferred. Ammonia or the alkali metal compound may conveniently be employed as an aqueous solution of, for example, ammonium hydroxide, sodium carbonate, etc., in the water component. When this method is employed, it is preferred to maintain a concentration of about 10 wt. percent or more of the ammonia or alkali metal compound in solution. The superatmospheric pressures employed at liquefaction 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 about 0.5 s.c.f. to about 175 s.c.f. per pound of carbon in the carbonaceous solid to be processed. Preferably, the amount of the reducing gas utilized is about 20 s.c.f. to about 75 s.c.f. per pound of carbon in the solid.

The process of the present invention may be employed in a batch type operation or a continuous type operation. When a batch operation is employed, fixed amounts of the carbonaceous solid, water, the ammonia-producing

compound or alkali metal compound and the reducing gas are charged to a suitable liquefaction zone, such as a rocking autoclave. The reactants are contacted in the liquefaction zone for a period of time sufficient to produce the desired amount of conversion and then the products are withdrawn from the liquefaction zone and the desired hydrocarbonaceous product is separated and recovered. A suitable contact time in a batch type operation is about 1 minute to about 600 minutes, preferably about 200 minutes to about 400 minutes. In a continuous operation, the carbonaceous solid, water, the ammonia-producing compound and the reducing gas are continuously charged to a suitable liquefaction zone and contacted therein. The reaction products are continuously withdrawn from the reactor and the desired hydrocarbonaceous 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 reactants charged per hour) of about 0.16 to about 1.0 may be employed, and about 0.5 to about 0.25 is particularly preferred.

The liquefaction zone or reactor utilized in the present process may be any suitable vessel or reactor which can maintain the reactants at sufficient temperature and pressure to provide liquefaction conditions. 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 of coal liquefaction. Preferably, the liquefaction zone includes means for admixing the reactants by stirring or other agitation.

The mixture recovered after the liquefaction step, in addition to the desired hydrocarbonaceous product, will contain water, which will generally be in a separate phase from the product. Most of the solids remaining in the mixture will be found in the water phase. Thus, the hydrocarbonaceous product may conveniently be separated from the water and from at least a major portion of any remaining solid residual materials such as ash, by simple mechanical separation of the phases. The water phase thus recovered may be recirculated to the liquefaction step for further use. Similarly, reducing gas which is not consumed during the liquefaction step may be recovered and recirculated to the liquefaction step. I have found that the present process actually does not consume hydrogen or carbon monoxide in substantial amounts, so that little fresh reducing gas is normally required in a continuous operation. The hydrocarbonaceous product may be further processed, for example, by petroleum refining methods such as cracking, to provide hydrocarbon fuels, aromatic chemicals for petrochemical uses, etc. When the process herein disclosed is utilized to treat the preferred carbonaceous solid, bituminous coal, the hydrocarbonaceous product recovered comprises a tarry material which is liquid at about 100° C. and has an ash content significantly lower than that of the raw bituminous coal. One of the major problems encountered in prior art coal liquefaction processes has been the separation of ash from the hydrocarbonaceous materials produced. The present process reduces the amount of ash in the hydrocarbonaceous liquefaction product sufficiently that further separation of solids may not be necessary, particularly since much of the solid residue remains in the water phase and is consequently very easily removed. This is particularly advantageous in view of the prior art methods which use a hydrocarbonaceous solvent in the liquefaction step, resulting in high contamination of the solvent with ash and other solids.

Liquefaction conditions may include the use of various catalysts to further enhance the liquefaction reactions in the present process. Suitable catalysts include metals from Group VIII of the Periodic Table of the Elements, particularly the sulfides of these metals, especially iron sulfide, nickel sulfide and cobalt sulfide. The above-noted metal sulfide catalysts may be utilized at a concentration

of about 0.001 wt. percent to about 10 wt. percent of the amount of carbonaceous solid material to be treated. A preferred concentration for such catalysts is about 0.1 wt. percent to about 2 wt. percent of the carbonaceous solid. In general, a catalyst may be employed by admixing it with the pulverized coal as a solid.

The hydrocarbonaceous product recovered from the liquefaction step is a tarry material melting at about 50° C. to about 200° C. comprising about 80–85 wt. percent carbon and about 6.5–8 wt. percent hydrogen, which is preferably further treated by conventional petroleum refining methods to provide hydrocarbon products. One particularly convenient method for recovering valuable components in the liquefaction product and simultaneously removing any remaining ash, carbonaceous solids, etc., is by extracting the hydrocarbonaceous product with an organic solvent. The solvents which may be employed are well known in the art. Examples of some suitable solvents which are particularly preferred include benzene, toluene, xylene, and similar C₆–C₁₂ aromatics, hexane, heptane and similar C₆–C₁₂ paraffins, ketones, C₆–C₁₂ cycloparaffins and alkylcycloparaffins, etc. Extraction conditions generally include a temperature of about 30° C. to about 300° C. and preferably about 50° C. to about 150° C. Superatmospheric pressure is desirable but not essential. After a contact time of about 0.1 minute to about 1500 minutes, the solvent and the product materials dissolved therein are mechanically or otherwise separated from whatever solid materials remain at the extraction conditions employed. The soluble hydrocarbons are then recovered by fractionation of the solvent or other conventional methods.

The following examples illustrate various embodiments and advantages of the process of the present invention. The examples are not intended to limit the broad scope of the present invention, and many other advantages and embodiments of the invention will be apparent to those skilled in the art from the description provided herein.

EXAMPLE I

A seam coal from Randolph Co., Bellville District, Ill., was analyzed to determine its average composition, which was found to be as shown in Table I.

TABLE I

	Wt. percent
Ash	10.18
Total nitrogen	1.32
Leco sulfur	3.34
Total oxygen	9.54
Free water	4.00
Volatiles	39.72
Carbon	64.45
Hydrogen	5.25
Dry ash	10.70

The coal was pulverized to provide particles sufficiently small to pass through a 200 mesh Tyler screen. One hundred grams of the pulverized coal and 400 grams of water were placed in an 1850 cc. rocking autoclave. The autoclave was sealed and sufficient hydrogen was introduced to provide a pressure of 70 atmospheres. No ammonia, alkali metal hydroxide or alkali metal carbonate was utilized. The contents of the autoclave were heated to a temperature of 350° C. A pressure of 310 atmospheres in the autoclave was observed. The contents were agitated at 350° C. for 6 hours, and then the autoclave was cooled to room temperature. The pressure was observed to be 62 atmospheres. The excess pressure was released and the remaining contents of the autoclave were removed. The effluent from the autoclave was observed to consist of a water phase and a hydrocarbonaceous phase. The hydrocarbonaceous phase, which solidified at about 100° C., was separated from the water phase by simple decantation and dried. The hydrocarbonaceous materials were then extracted with benzene. It was found

that the benzene soluble fraction of the hydrocarbonaceous phase contained 30 wt. percent of the carbon in the original 100 grams of coal charged to the autoclave.

EXAMPLE II

One hundred grams of the same pulverized coal employed in Example I was placed in the same autoclave used in Example I. No water and no salts were employed in this run. One hundred cc. of xylene was placed in the autoclave with the coal and the autoclave was sealed. Sufficient hydrogen was charged to the autoclave to produce a pressure of 70 atmospheres. The contents of the autoclave were agitated at a temperature of 350° C. for six hours. The contents were then cooled and the excess pressure was released. After separation of the xylene solvent from the hydrocarbonaceous product and drying, the product was extracted with benzene in a manner identical to that used in Example I. It was found that 31 wt. percent of the carbon in the original 100 grams charged to the autoclave had been converted to benzene soluble hydrocarbons.

EXAMPLE III

In order to demonstrate the superiority of the process of the present invention over the methods employed in Examples I and II, 100 grams of the pulverized coal described in Example I was placed in the same autoclave. Four hundred cc. of water and 50 grams of sodium hydrogen carbonate were also placed in the autoclave. The autoclave was sealed and sufficient hydrogen was introduced to raise the pressure to 70 atmospheres. The contents of the autoclave were then stirred at 350° C. for six hours, after which the autoclave was cooled and excess pressure was released. The benzene soluble product, recovered in exactly the same manner as employed in the foregoing Examples I and II was found to contain 48 wt. percent of the carbon in the 100 grams of coal originally charged to the autoclave. From comparison of Example III with Examples I and II it is apparent that the presence of both water and the alkali metal salt is necessary to attain a high degree of conversion as was achieved in Example III. For instance, the method of the present invention, employed in Example III produced 37% greater conversion than Example I where no alkali metal salt was used and produced 35% greater conversion than the method of Example II where no water was used.

EXAMPLE IV

The following procedure was employed to demonstrate the substantially equivalent results obtained when ammonia was substituted for the alkali metal carbonate employed in Example III. Fifty grams of the pulverized coal used in Example I was placed in an 850 cc. rocking autoclave with 100 cc. of water and 100 cc. of a 28% ammonium hydroxide solution. The autoclave was sealed and sufficient carbon monoxide was introduced to provide a pressure of 70 atmospheres. The contents of the autoclave were heated to 350° C. and agitated at that temperature for 6 hours. The pressure was observed to be 410 atmospheres. The autoclave was then cooled to room temperature and the excess pressure released. The remaining contents were removed and the water phase thereof was separated by decantation. The hydrocarbonaceous phase was dried and extracted with benzene. The benzene soluble hydrocarbons were found to contain 45 wt. percent of the carbon in the coal originally charged to the autoclave, or slightly less than was obtained using sodium hydrogen carbonate as in Example III. The yield obtained using ammonia compared very favorably to the yields of Examples I and II, achieving 33% greater conversion and 31% greater, respectively, than these two runs.

EXAMPLE V

Having shown by Examples I through IV that the presence of water and an alkali metal salt or ammonia is

essential to obtain the desired conversion, and that the presence of an organic solvent, as in Example II, did not effect the conversion significantly, a run was undertaken to demonstrate that the presence of a reducing gas was also essential. Fifty grams of the coal described in Example I was charged to the autoclave used in Example IV along with 100 cc. of water and 100 cc. of the same 28% ammonium hydroxide solution utilized in Example IV. Without introducing any reducing gas, the autoclave was sealed and the contents were agitated and heated to 350° C. The pressure observed was 202 atmospheres. After 6 hours the autoclave was cooled and the contents were removed. The water phase was separated by decantation, and the hydrocarbonaceous product was dried and extracted with benzene as in Example IV. It was found that only 5 wt. percent of the carbon in the original charge of coal to the autoclave was present in the benzene soluble product. The necessity for employing a reducing gas in the process of the present invention is apparent from this result.

EXAMPLE VI

In order to demonstrate the efficiency of a mixture of hydrogen and carbon monoxide as the reducing gas in the present process, the following operation was performed. Fifty grams of the pulverized coal described in Example I were placed in the autoclave described in Example IV. One hundred cc. of the 28% aqueous ammonium hydroxide solution were also charged to the autoclave. The autoclave was sealed and sufficient carbon monoxide was charged to the autoclave to provide a pressure of 35 atmospheres. Sufficient hydrogen was then charged to provide a hydrogen partial pressure of 35 atmospheres and a total pressure of 70 atmospheres. The contents of the autoclave were heated to 350° C., and a pressure of 388 atmospheres was observed. The contents of the autoclave were maintained at 350° C. and agitated for six hours, after which the contents of the autoclave were cooled to room temperature and excess pressure released. The contents of the autoclave were removed and decanted into a water fraction and a hydrocarbonaceous fraction. The hydrocarbonaceous fraction was dried and extracted with benzene. The extracted materials were found to contain 43% of the carbon in the coal originally charged to the autoclave.

Use of a hydrogen-carbon monoxide mixture provided a conversion of substantially the same degree as the use of pure hydrogen or pure carbon monoxide.

EXAMPLE VII

In order to demonstrate further the desirability of utilizing water in the liquid phase, an operation was undertaken using a mixture of hydrogen and carbon monoxide at lower pressure. One hundred grams of the pulverized coal described in Example I was charged to the 1850 cc. rocking autoclave along with 100 cc. of water and 100 cc. of the 28% ammonium hydroxide solution. The autoclave was sealed and sufficient hydrogen and carbon monoxide were introduced to provide 10 atmospheres partial pressure of each gas, with a total pressure of 20 atmospheres. The contents of the autoclave were agitated at 350° C. for 6 hours, after which the autoclave was cooled to room temperature and excess pressure was released. The contents of the autoclave were removed and the water phase was separated by decantation. The hydrocarbonaceous phase was dried and extracted with benzene. It was found that only 11 wt. percent of the carbon in the original charge of coal to the autoclave had been recovered in the benzene soluble fraction.

EXAMPLE VIII

In order to demonstrate the non-equivalence of salts of the alkali metals other than carbonates and hydroxides, the following operation was undertaken using sodium sulfate. One hundred grams of the pulverized coal described

in Example I was placed in the 1850 cc. rocking autoclave, and 100 cc. of water, 100 grams of Na_2SO_4 and 100 cc. of xylene were also charged. The autoclave was sealed and pressured with hydrogen to 70 atmospheres. The contents of the autoclave were agitated at 350° C. for 6 hours and then the autoclave was cooled to room temperature and excess pressure was released. The contents were removed and the water phase separated by decantation. The hydrocarbonaceous phase was dried and extracted. The benzene soluble hydrocarbons were found to contain 26 wt. percent of the carbon originally charged to the autoclave in the coal. It is apparent from the low conversion achieved using sodium sulfate, that it is not equivalent to the carbonate salt employed in Example III or to ammonia as employed in Example IV.

EXAMPLE IX

The following operation was undertaken to determine the effect produced by using an organic solvent, in this case xylene, with the water, ammonia and reducing gas.

In two separate operations, 100 grams of the pulverized coal described in Example I were placed in the 1850 cc. rocking autoclave. 100 cc. of water, 100 cc. of an aqueous 28% solution of ammonium hydroxide and 100 cc. of xylene were also charged to the autoclave in both runs. The autoclave was then sealed. In the first run, sufficient hydrogen was introduced to increase the pressure to 70 atmospheres. In the second run, sufficient carbon monoxide was charged to provide 70 atmospheres pressure. The contents of the autoclave were heated to 350° C. in both runs. A pressure of 246 atmospheres was observed in the run using hydrogen, and a pressure of 316 atmospheres was observed in the run using carbon monoxide. The contents of the autoclave were agitated for 6 hours at 350° C. in both runs. The autoclave was then cooled to room temperature and the excess pressure released. The remaining contents were removed and decanted into a water fraction and a hydrocarbonaceous fraction. The hydrocarbonaceous fraction was dried and solvent extracted with benzene. In the run using hydrogen as the reducing gas, the extracted materials contained 46 wt. percent of the carbon in the original 100 grams of coal charged to the autoclave. In the run using carbon monoxide, 45 wt. percent of the original coal carbon was contained in the extracted material. The foregoing demonstrates that using an aromatic hydrocarbon solvent has substantially no effect on the degree of conversion achieved using the process of the present invention.

The foregoing examples clearly demonstrate the superior conversion achieved using the processing conditions and components of the present invention, and indicate a preferred mode of operation of the present process when a batch reaction scheme is employed. Modification of the operation to a continuous type operation, etc., will be obvious to those skilled in the art.

I claim as my invention:

1. A process for de-ashing and liquifying coal which comprises contacting the coal with from about 100 wt. percent to about 1000 wt. percent of water, a reducing gas selected from the group consisting of hydrogen, carbon monoxide and a mixture of hydrogen and carbon monoxide, and a catalytic compound selected from the group consisting of ammonia and alkali metal hydroxides and carbonates at a temperature of from about 200° C. to about 370° C. and a pressure of at least about 20 atmospheres but below about 400 atmospheres and sufficient to maintain said water at least partially in the liquid phase, separating the resultant mixture into a hydrocarbonaceous phase and a solids-containing aqueous phase, and recovering a hydrocarbon liquefaction product from said hydrocarbonaceous phase.

2. The process of claim 1 wherein the liquefaction product is recovered from said hydrocarbonaceous phase by solvent extraction.

3. The process of claim 1 wherein said catalytic compound comprises about 0.1 wt. percent to about 1000 wt. percent of said coal and said alkali metal is selected from sodium and potassium.

4. The process of claim 1 wherein said reducing gas comprises hydrogen. 5

5. The process of claim 1 wherein said reducing gas comprises carbon monoxide.

References Cited

UNITED STATES PATENTS

3,642,607	2/1972	Seitzer	-----	208—10
3,687,838	8/1972	Seitzer	-----	208—10

DELBERT E. GANTZ, Primary Examiner

V. O'KEEFE, Assistant Examiner