CHEMISTRY LETTERS, pp. 649-652, 1986.

LIQUID FUEL PRODUCTION FROM ETHANOL FERMENTATION STILLAGE

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Liquid fuel was directly produced from ethanol fermentation stillage. When stillage was treated with sodium carbonate under pressure of nitrogen at 300 °C, oily products separable from an aqueous phase were obtained. The yield of heavy oil having a heating value of 35 MJ/kg attained about 50% and the energy recovery of heavy oil exceeded 75% of starting material.

Recently the production of ethanol through fermentation process has been increasing in terms of alternative energy in many countries. Also in our country the production of ethanol including beverage alcohol has been ascending gradually. In ethanol industry, however, stillage which is an aqueous organic waste from fermentation and distillation processes is being produced as an unavoidable by-product. Only a small part is utilized as fertilyzer or cattle feed after dewatering, but the most part is wasted or disposed of without use. It is generally accepted that about 10 times as much stillage as product ethanol by volume is discharged.1) As the production of ethanol increases, stillage will become a serious problem with respect to environmental impacts. In Brazil, for example, the production of ethanol from biomass fermentation will be about 10 million kl in 1985. The amount of stillage co-produced from distillation process will be vast and, thus, an important effort has to be undertaken to solve this problem.

In our previous papers,2-4) it was demonstrated that woody materials can be efficiently converted to heavy oil by reacting them with alkali metal salt as catalyst in an aqueous phase under pressurized inert gas. In the present study, this aqueous phase liquefaction was applied to stillage for the production of liquid fuel. Same reaction conditions giving highest yields for woody materials were adopted.

Usually stillage has a high water content in the range of 95-98%, the rest being dry solid like protein, fat, fiber, carbohydrate, and ash. In this experiment, the stillage having a water content of 95%, available from fermentation of rice, was dewatered to 74.0% manually using a nylon mesh net. The stillage is characterized in Table 1. The analyses of chemical and elemental compositions were made outside the laboratory (Japan Food Research Laboratories and Fuel Society of Japan). The amounts of protein, fat, fiber, and ash were measured by Kjeldahl method, Soxhlet's extraction, improved Henneberg-Stohmann method, and ignition at 550 °C, respectively. The amount of carbohydrate was determined by difference. The analyses of elemental composition and the measurement of heating value were done according to JIS method.

Table 1. Composition of stillage[a)]

Chemical composition / wt%[b)]				
Protein	Fat	Fiber	Carbohydrate[c)]	Ash
24.5	2.8	0	71.8	0.9
Elemental composition / wt%				
C	H	O[d)]	N	S
52.00	7.70	33.60	5.90	0.80

a) The water content of stillage used was 74.0 wt%.
b) On a dry weight basis.
c) Calculated by difference.
d) Calculated by difference.

The reaction was performed in a 300 ml autoclave (SUS 304). Stillage (60.8 g, water content 74.0 wt%) and sodium carbonate (1.58 g) were charged into the autoclave. After sealing the autoclave and flushing with nitrogen, nitrogen was added to a pressure of 12.0 MPa. The temperature was then raised to 300 °C at the heating rate of about 10 °C/min. Though the vapor pressure of water is expected to increase with the rise in temperature, the total pressure was successfully kept at 12 MPa by releasing the overpressure through a back pressure regulator (TESCOM 26-1723-24) into a gas reservoir. After the temperature attained to 300 °C, the autoclave was cooled down immediately to room temperature. The volume of gas evolved was measured by a gas meter and its composition was determined by a gas chromatograph. The autoclave was then opened and the reaction mixtures were poured into a glass bottle.

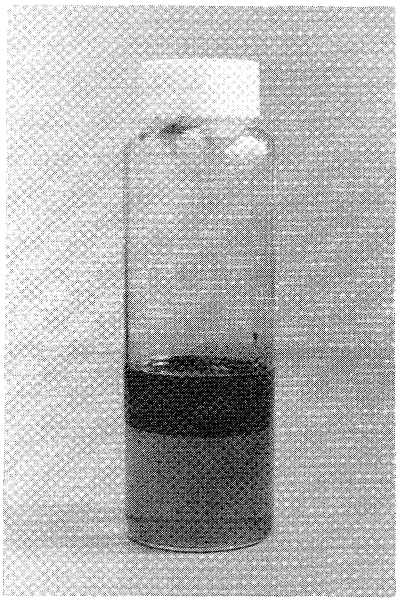
Fig. 1. Reaction mixtures after 30 min.

Just after the reaction mixtures were poured into the bottle, they looked homogeneously muddy. However, they gradually began to separate into two phases. Figure 1 shows the reaction mixtures after they stood in air for 30 min. Obviously, the upper oily phase was separated from lower aqueous phase. This quite easy method of separation has not been reported so far in the field of liquefaction of biomass and organic wastes. A rough estimation indicates that the water content of upper phase is 40-50%, suggesting that the upper phase is possibly combustible without further treatment. In this experiment, however, the upper phase was treated according to the similar procedure applied to extracting heavy oil from woody materials, though dichloromethane was used instead of acetone. The upper layer was dissolved in dichloromethane. After the residue was separated by filtration, the filtrate was exhaustively extracted with the same solvent. Then the dichloromethane was evaporated from the extract using a rotary evaporator. A dark brown viscous material (referred to as heavy oil hereafter) was obtained in this manner. If liquefaction was performed without addition of sodium carbonate, the reaction mixtures were not separated into two phases. In this case, the yield of heavy oil, which was extracted from the reaction mixtures by the same procedure as mentioned above, was less than 20%.

Table 2. Material balance of liquefaction

Starting material			Product distribution a)		
Stillage	(60.80 g)		Heavy Oil	(7.72 g)	49.2%
org. material	(15.70 g)	25.8%			
inorg. material	(0.10 g)	0.2%	Solid Residue	(1.02 g)	
water	(45.00 g)	74.0%	org. material	(0.87 g)	5.5%
Sodium carbonate	(1.58 g)		inorg. material	(0.15 g)	
			Aq. Material	(51.14 g)	
			org. material	(3.47 g)	22.1%
			inorg. material	(1.75 g)	
			water	(45.92 g)	
			Gas	(2.51 g)	16.0%
			Loss	(1.10 g)	7.2%

a) Pecentage in the product distribution is on the organic basis of starting material.

Table 2 summarizes the results of liquefaction of stillage. From this Table, it can be seen that the yield of heavy oil was 49.2% on the basis of organic compounds [=(weight of heavy oil/weight of organic material in stillage) x 100]. The organic components in products were distributed also in solid residue, aqueous phase, and gas. Though the gas was mainly composed of carbon dioxide, it was regarded as an organic component for convenience. Loss of organic material may be due to vaporization of lighter hydrocarbons in addition to experimental error. Interestingly, the inorganic materials, that is, a minor portion of ash in stillage plus sodium carbonate as catalyst, were almost recoverd in the aqueous phase not in the solid residue. The pH of the aqueous solution was about 9.0, indicating that amines were formed by the degradation of protein during liquefaction. In contrast, the aqueous phase was highly acidic (pH 3.5-4.5) in the case of liquefaction of woody materials due to the formation of acidic compounds.

Table 3 shows the properties of heavy oil. Compared with the composition of stillage in Table 1, the content of oxygen was greatly reduced, and for nitrogen and sulfur their contents were also reduced to about one-half, taking into consideration that the heavy oil yield was 49.2%. Since the heating value of stillage is 22.6 MJ/kg, the energy recovery [=(heating value of heavy oil/heating value of starting material) x 100 = (35.0 x 7.72/22.6 x 15.7) x 100] is 76.2. This suggests that more than 75% of energy of starting material can be recovered in the form of heavy oil. The heavy oil is probably composed of a number of complex organic compounds. A further study will be needed for their identification.

Table 3. Properties of heavy oil

Heavy oil extracted						
Elemental composition / wt%					Water content wt%	Heating value MJ/kg
C	H	O$^{a)}$	N	S		
70.60	9.24	13.53	5.81	0.82	1.60	35.0

a) Calculated by difference.

With respect to the mechanism of liquefaction, no clear explanation has not yet been proposed so far. The stillage is mainly composed of protein and carbohydrate as given in Table 1. As to protein, it is well known that it is readily hydrolyzed into smaller fractions under alkaline environment. Russell and coworkers$^{5)}$ reported that aromatic compounds are produced by condensation and cyclization of low molecular weight aldehydes and ketones formed by decomposition of carbohydrate in an aqueous alkaline solution. These fractions which are dichloromethane soluble seem to contribute to the production of heavy oil.

As far as we know, the present result that an oily phase was separated from an aqueous phase is the first finding in liquefaction process of biomass and organic wastes. It is recently reported that Combustion and Fuel Research, Inc. and Battelle Pacific Northwest, both investigating catalytic sludge conversions, are confronted with the problem of non-separation of oil/water due to severe product emulsification.$^{6)}$

In conclusion, it should be emphasized that heavy oil having a heating value of 35 MJ/kg can be produced efficiently from ethanol fermentaion stillage in an alkaline solution accompanied by the phase separation. This finding will surely contribute to ethanol fermentation process in terms of not only water pollution control but also energy recovery from aqueous organic materials.

The authors thank Director-General Dr. Etsuro Nakamura of the National Research Institute for Pollution and Resources for his valuable discussion throughout this work.

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(Received January 7, 1986)