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Study on the Multicomponent Catalytic Liquefaction Technology of Corn Stalk Features†

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Using rich corn straw resources as raw materials, which come from the northeast China. It is liquefied by multicomponent compound solvent, testing the reaction time, reaction temperature and the dosage of the catalyst. These process conditions are inspected for the liquefaction of the corn stalk and the chemical test and instrumental analysis used for the liquefied products. Finally the best process conditions have been obtained. The result shows that the liquefied product contains phenols, aldehydes, the double bond containing compound and carboxylic acids. These substances can be converted into the corresponding ethers and other high molecular compound, which can be applied to produce biodegradable materials and chemicals product in the industries of plastic, construction, insulation and so on. Crop straws could be converted into industrial raw material by catalyzed liquefaction. These industrial raw materials will replace the fossil resources which have dried up and product polymer materials which are good for the environment. Alternative petrochemical from the liquefaction product will reduce the pollution of the agricultural waste straw on tone environment as well as the consumption of the fossil resources. Given the biological degradation, there is a deep significance on the environment and sustainable development. At the same time, the liquefaction of corn stalk can reduce the dependence on fossil fuels and makeup the economy with single energy products. The market potential is tremendous and strategic importance is obvious.

Keywords: Corn stalk, Composite solvent, Liquefaction, Technology.

INTRODUCTION

Biomass is the only renewable carbon resource; it can be converted into conventional liquid fuel and other chemical raw materials or products. The utilize technology of biomass and the available way of fossil fuels have high compatibility. The native has much corn stalk biomass resources; every year, the production of corn stalk is 250 million tons. In China, the available way of corn stalk is still in the lower level lead to the serious waste of corn stalk resource and environmental contamination and the pollution caused by straw burning is one of the pollution problem[1]. Therefore, using straw of reasonable and efficient is one of high importance for the national economy sustainable development and environmental protection. Under certain conditions cellulose, hemicelluloses and lignin of corn stalk are converted into a set reactive liquid substances, preparation of polymer materials can be used as raw material, is one of the high value added utilization pathways of straw resources. Thus, the production cost of materials can be reduced and the problem of resource can also be solved[2]. Atmospheric liquefied of biomass is that biomass put into liquefaction, under the condition of normal pressure; biomass can convert into the liquid mixture that the relative molecular mass distributed widely. This process is referred to as atmospheric liquefied of biomass and this way has many features, for example, mild reaction conditions, simple equipment and so on. The features of the product can replace traditional petrochemical chemicals. For the domestic common agricultural waste-corn stalk is liquefied to polyhydric alcohols. We based on their liquefaction performance contract research, choose the appropriate solvents as liquefaction. The liquefaction product has been carried on the preliminary analysis and lay the foundation for the subsequent high value utilization. It has many characteristics, such as process simple and easy to large-scale industrialized production. Therefore, this becomes a research hotspot in the field of biomass. By the wide attention of scholars both at home and abroad and in-depth study and it has made particular progress.

EXPERIMENTAL

Corn stalk obtained from Jilin city suburbs. First the corn stalk cut into small sections, and then the mill will grind its to

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3 mm, placed in the store at room temperature; Ethylene glycol, polyethylene glycol (200) (PEG200) and glycerol, they are all analytically pure[6].

6202 small model high speed mill, 101 A-Z drying oven, ALC-2104 electronic balance, JJ-1 close reinforcing electric mixer, R-202 rotary evaporation apparatus, W201B numerical control constant temperature water bath pot, EQUINOX55 Bo state transform infra-red spectrometer.

Liquefaction of corn stalk: First put corn stalk powder in three mouth bottles which has stirring effect, the condensation reflux pipe and thermometer; then join liquefaction and catalyst, the catalyst is concentrated sulfuric acid, homogeneous mixing; at last put three mouth bottles in the constant temperature oil bath to react of liquefaction (experimental device Fig. 1), when the temperature rises to a specified temperature and starting time. All the three bottles will set in the cold water to termination reaction after the completion of the reaction[7].

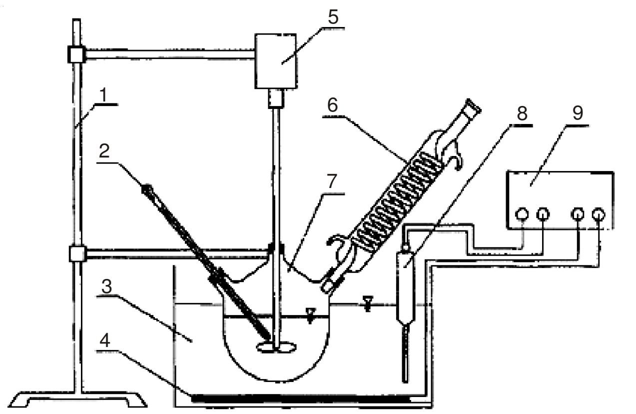

Fig. 1. Installation drawing of straw liquefied experimental. 1. Hob Table- 2. Thermometer 3. Constant temperature oil bath 4. Heating resistance 5. Agitator 6. Condenser pipe 7. Three-flask 8. Temperature sensor 9. Relay

Calculation of liquefaction yield: Take about 2 g of the liquefied products, with about 20 mL dioxane and water mixture (dioxane: water = 8:2) put in 80 ºC water bath to pot insulation 20 min with stirring constantly. First mixed liquid is filtered by the fabric's funnel pad filter paper (medium speed quantitative filter paper); then a mixture of dioxane and water should be used to rinse repeatedly filtrate until filtrate colourless. Residue together with the filter paper can be put in the oven to 105 ºC drying 4 h, after constant quality, measuring residue. Liquefied rate:

$$Y = 1 - \frac{M_a}{M_e}$$

Type: Y-liquefied rate (%), M_a-raw material quality (g), M_e-quality of residue (g).

Analysis of raw material: The chemical composition analysis of corn stalk mainly includes components analysis, cellulose, hemicelluloses and lignin.

Elemental analysis: Using the Vario MICRO type element analyzer which is produced by the Germany elemental company to do the quantitative determination of elements, the main measure includes four kinds of elements: C, H, O and N, analysis of accuracy is 0.1 %. As a result, the figures of the content of C, N, H are derived from the instrument, ignoring the microelement that content low relatively and its total element content minus C, H, N approximately used as the figure of the O element.

Determination of sample moisture content: 105 ºC drying method: Taking the straw out and sieving mixing it, quartering sampling at around 100 g set in drying to constant weight aluminum box (m_0) weighing (m_1) and then 105 ºC oven drying for 24 h, cooling in the dryer, weighing (m_2). After weighing, dry, the material again in the dry, take out after 1 h, cooling in the dryer, weighing (m_3). So repeatedly, until the volumes of m_3 differ by 0.002 g from m_3's volumes, after drying, calculate the content of water. Take out two parallel specimens from each sample, do the determination, with the average as the calculation results.

The calculation of moisture content:

$$\text{Moisture content } (\%) = \frac{(m_1 - m_3)}{(m_1 - m_0)} \times 100\ \%$$

Dry matter content (%) = (1 - Moisture content) × 100 %

Determination of ash: The determination of ash content in raw materials (GB/T742-2008): Ash % = 100 × (total weight after ashing – the weight of porcelain dish)/dry sample weight.

Lignin content measurement: The determination of lignin content in maize straw in accordance with the (GB/ T2677.8-1994).

Determination of palm fiber: Corn stalk palm fiber content determination (GB/T2677.10-1995).

Determination of cellulose: The determination of cellulose content that comes from the corn stalk uses concentrated sulfuric acid hydrolysis process[3].

Determination of acid value: Automatic potentiometric testator, models: titroLine alpha plus, factory: German SCHOTT.

Fourier transform infrared spectrometry of liquefaction products: Maize straw, liquefied products by KBr tablet method; Liquefied agent using reflection process, the use of Germany Brooke instrument company Fourier transform infrared spectrometer (model for EQUINOX55) test, the wavelength range is 4000-400 cm^{-1}.

Liquefaction products GC-MS analysis: Used the gas chromatography/mass spectrometry (GC-MS), JHP-33, which come from Hewlett Packard companies in the United States to analysis the material construction of liquefaction oil. After the sample is dissolved in acetone junior, inject in HP-5 ms chromatographic column (30 m × 0.05 µm × 0.32 nm (i,d)) type capillary column and hydrogen flame ion detector; WSC gas chromatography workstation, testing conditions: 40 ºC (5 min) to 280 ºC (20 min), heating rate: 20 ºC/min, injection port 270 ºC and ion chamber 270 ºC; the carrier gas velocity 30 mL/min, sample quantity 0.1 µL, mass spectrometry interface temperature 270 ºC, ion source temperature 220 ºC, quadrupole temperature 100 ºC, mass spectrum scan range 30-500 amv, the process of sampling is fractional sampling, fractionation than 30:1, head pressure 15 psi, sample quantity 0.1 µL.

RESULTS AND DISCUSSION

Composition analysis of biomass raw material: This experiment uses mainly the rich corn straw resources as raw materials, which come from the northeast China. The chemical composition of corn stalk includes cellulose, hemicelluloses, lignin and other components. Through the study on the basis of raw material composition can make a basic understanding of material properties, this will lay the foundation for subsequent processing and utilization. Corn stalk material contain cellulose 43.52 %, hemicelluloses 25.94 %, lignin 30.33 %, ash 1.21 % and water 4.31 %; elemental study results: O 48.2 %, C 45.4 %, H 5.3 %, N 1.1 %.

Different solvent ratio liquefaction effects: Polyols can make cellulose, hemicelluloses and lignin which comes from corn stalk degrade fully. Reaction condition is set to: reaction temperature is 160 ºC, reaction time is 1 h, catalyst selection is 98 % sulphuric acid glycol. Catalytic dosage and liquefied dosage volume ratio are 3:100, the ratio of liquefaction dosage and raw material consumption are 5:1. On this condition liquefied[4], in first, using single glycol, PEG200 and glycerol as liquefaction; then according to different mixing ratio, selecting respective glycol, glycerin and PEG200 to constitute complex liquefaction; At last, inspects liquefaction effect of straw as shown in Table-1.

TABLE-1
LIQUEFACTION EFFECT OF DIFFERENT SOLVENTS

Reagent		Liquefied rate (%)
Ethylene glycol		82.0
Glycerol		83.5
Polyethylene glycol		88.0
Ethylene glycol-glycerol-polyethylene glycol (volume ratio)	1:3:1	82.0
	1:1:3	83.5
	1:2:2	89.5
	1:1:1	90.5
	2:2:1	88.9
	2:1:2	86.5
	3:1:1	82.6

From Table-1, using three kinds of liquefaction alone, the liquefied effect is PEG200 > glycerol > glycol. When PEG200, ethylene glycol, glycerin mixed solvent volume ratio of the three components will closer, the liquefaction result will more greatly, so the best proportion solvent mixture of three components: 1:1:1[5]. Under the condition of optimum liquefaction, after the liquefaction of corn stalk get black sticky liquid product for instrument analysis. Liquefaction product basic characteristics are given in Table-2.

TABLE-2
PROPERTIES OF LIQUEFIED OIL

Properties	Liquefied oil
Moisture (%)	3.84
Viscosity (maps)	980
Acid value (mg/g)	2.3
Hydroxyl value (mg/g)	862

Liquefaction product of infrared spectrum analysis: The experiment uses Fourier infrared spectrometer which is produced by the German Burke business and the design is EQUINOX55.The corn stalk and liquefaction product were analyzed, respectively (Fig. 2). Compared with raw material absorption peak, liquefied products in 2922 cm^{-1} place the peak intensity is weakened and this area is methyl and methylene stretching vibration. Moreover 1101 cm^{-1} place absorption peak is C=O stretching vibration of cellulose and hemicelluloses. The 2921 cm^{-1} position in raw materials which are caused by C-CH_2-C saturation alkyl C-H stretching vibration lead to the absorption peak, in the liquefied products, strengthening the absorption. Ether bond asymmetric stretching vibration absorption peak also strengthened, this suggests that in the response, the C-O of lignin aromatic ring connected the break under the effect of liquefaction and liquefied products have parts of the cellulose and hemicelluloses. Liquefied products in 3421 cm^{-1} place absorption peak is strengthened, this is stretching vibration of associating O-H and explain that in the product, hydroxyl compound increased. It is difficult that biomass used directly and the cellulose, hemicelluloses and lignin which come from biomass is very stable and used difficultly in usually state. The study results show that after biomass is liquefied, the three main components are degraded, liquefaction product contains various active functional groups and the following can be high value used as energy or material.

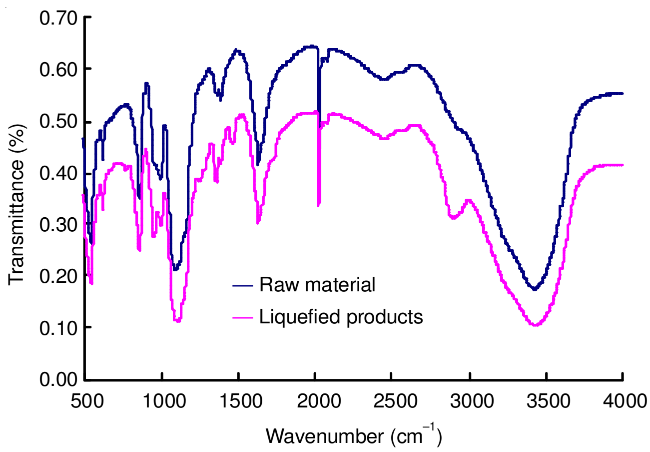

Fig. 2. Infrared spectra contrast of raw material and liquefied products

Liquefied oil composition analysis: By GC-MS analysis of liquefaction oil (Fig. 3 and Table-3), liquefied oil mainly include acid, ester, alcohol, ether, acetone, phenolic substances, most of substances are cyclic annular and branched chain structure; polyester polyols mainly include 3-methoxy-4-hydroxy benzoic acid ethyl ester, 4-carbonyl pentanoic acid butyl ester, 3-methoxy-4-hydroxy benzoic acid ethyl ester and 2,3- dimethyl-2-hydroxy-1,4-succinic acid diethyl ester, these substance stem from acid of sawdust decomposition and then with alcohol happened esterification reaction. Polyether type polyols mainly include ethylene glycol mono-ethyl ether, the triethyl glycerin ether and phenol of aromatic species, these substances lie in the chemical reaction among raw materials and corn stalk degradation of hydroxyl active substances occurred condensation reaction.

Conclusion

The best corn stalk liquefaction process conditions: Single use glycol, PEG200 and glycerol liquefier, liquefied effect for PEG200 > glycerol > glycol; in the same conditions, ethylene glycol, PEG200 and glycerol solvent for mixing proportion of cooperation liquefaction than single solvent for liquefaction obvious results. It is concluded that the best technological conditions for reaction temperature is 160 ºC, reaction time is

TABLE-3
MAIN COMPONENTS IN LIQUEFIED OIL OF CORN STALK

Composition	Retention time (min)	(wt %)	Quality (%)
2-Ethyl-4-methyl-1,3-two tetrahydrofuran	6.336	0.641	38
2,2-Dimethyl-4-methanol-1,3-two oxygen heterocyclic pentane	6.834	7.770	78
3-Ethoxy-1,2-propylene glycol	7.776	26.857	78
1,3-Two ethoxy propanol	9.053	8.431	80
4-Carbonyl pentanoic acid ethyl ester	10.523	6.511	95
Triethyl glycerol ether	10.966	0.687	83
2-Methoxy phenol	11.302	0.769	93
4-Carbonyl pentanoic acid butyl ester	22.813	2.403	72
2-Ethyl butyrate	23.295	1.864	36
2,2-Two ethoxy ethyl propionate	23.487	0.913	46
3-Methoxy-4-hydroxy-benzene acetic acid	23.796	0.761	55
2,3-Dimethyl-2 - hydroxy-1, 4-succinic acid diethyl ester	24.207	1.117	35
3-Methoxy-4-hydroxy-benzoic acid ethyl ester	24.371	3.849	90

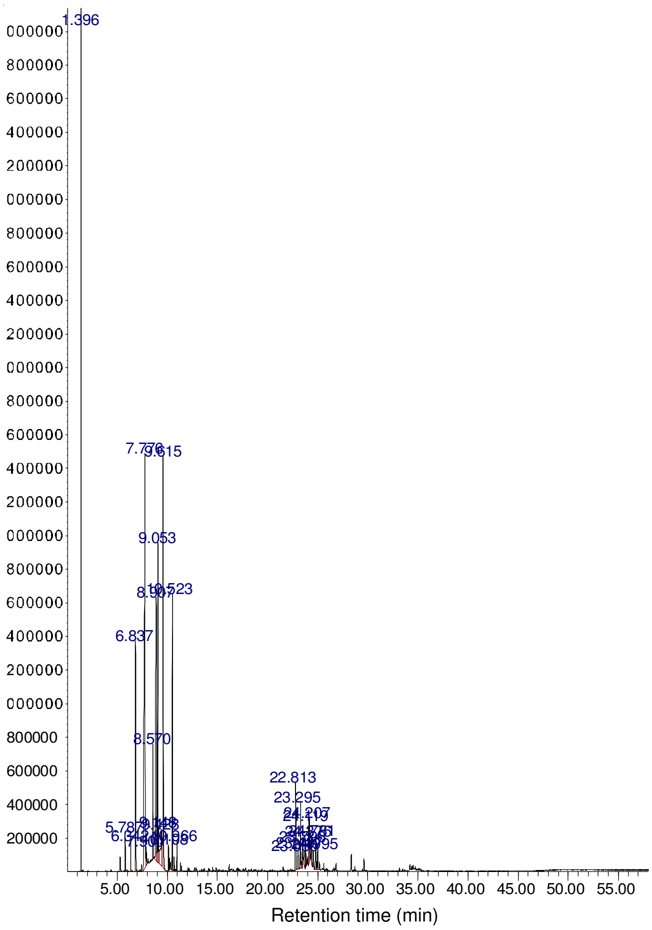

Fig. 3. GC-MS analysis of liquefied oil of corn stalk

1 h, catalyst amount to total liquefied agent of 3 %; on the product study results show that the solvent liquefied corn straw can be effective degradation of cellulose, hemicelluloses and lignin for using subsequent processing to provide the possibility. In this condition of getting liquefied products, through infrared spectrum analysis, the liquefied oil contains a large number of hydroxyl and ester base functional groups; by GC-MS analysis shows that the liquefied oil actually contains many kinds of ring formation or branched chain structure; this structure can be used in a high value utilization.

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