The Experimental Research on Efficient Process of Bio-aromatics Production

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Abstract. The process research of biomass catalytic cracking for production of bio-aromatics was performed with a 50kg/h riser reactor designed by China Energy Conservation and Environmental Protection Group (CECEP). The catalyst was chosen on the basis of a previous study, were Zn²⁺ exchanged zeolite type catalyst supplied by China University of Petroleum. Via analysis of the liquid product collected in different temperatures, influence of reaction temperature on the yield of bio-aromatics is investigated in this paper, the high yield of aromatics form corn stalk is 15.5wt%, obtained at 500℃, while gas yield is 33.5wt%. The creative process described in this paper provides a new efficient and easily scaled method for bio-aromatics production, also could be available to industrial pilot plant design studies.

1. Introduction
Aromatics are the most basic raw materials in the organic chemical industry. They are mainly derived from petroleum and coal tar. Benzene, toluene and xylene of aromatics are important basic raw materials for petrochemical industry. The largest use of benzene is to produce styrene, the second use is hydrogenation of benzene to produce cyclohexane, which is used to produce nylon through the process of cyclohexane oxidation-cyclohexanone-caprolactam. The largest amount of xylene is p-xylene (PX). PX can be made into terephthalic acid by high temperature oxidation. It is the main raw material of synthetic polyester (polyester). In the world's synthetic fibre production, polyester accounts for more than 60% [1]. Polycyclic aromatics can also be used to produce aerodynamic fuels with high energy density via hydrotreatment and hydro-isomerization process.

The whole process of fossil raw materials to aromatics is complex, and with the large consumption of fossil fuels, along with the price of crude oil continually rising, the cost of the chemical industry is also rising. In addition, a large number of by-products and other toxic gases and wastes are generated in the petroleum refining process, which seriously pollutes the environment. Therefore, the search for renewable and clean alternative materials and development of bio-aromatics producing process has attracted the attention of many companies and research institutions all over the world.
Agricultural and forestry waste biomass is composed of cellulose, semi-cellulose and lignin. Due to its special molecular structure, a variety of organic chemicals and fuels can be produced through appropriate catalytic conversion process. The development and application of biomass-to-aromatics process can not only reduce the dependence of aromatics production on fossil materials, but also be an alternative process to alleviate the scarcity of global petroleum resources.

Biomass-to-aromatics technology refers to the cracking and type-selective catalytic reaction of biomass feedstock under the action of a catalyst to produce liquid, gas, and solid products, wherein the main component of the liquid product is aromatics. Zeolite-based catalysts exhibit the highest aromatics yield for biomass catalytic pyrolysis due to its pore size, low internal pore volume and structure [2-7]. The bio-aromatics yield can be increased further by the addition of metal oxides to the zeolites [8-10]. Yan Zhao used HZSM-5 zeolite as catalyst in the poplar fixed-bed cracking process, and acquired over 20wt% aromatics yield [11]. Pranav U carried out catalytic fast pyrolysis of cellulose in a bubbling fixed-bed reactor, obtained a maximum of around 18wt% yield of aromatics [12]. Huiyan Zhang designed an inner loop fluidized bed to complete process of biomass catalytic pyrolysis, obtained around 14wt% yield of aromatics [13].

At present, most researchers use electrically heated fixed-bed and bubbling fluidized-bed as biomass catalytic pyrolysis reactor. The catalyst cannot be continuously regenerated after coking inactivation, which may lead to decrease catalytic reaction effect. Electric heating cannot supply the heat absorbed by the reaction in time, causes the decreasing of reaction temperature, affects product quality and yield. In this paper, the design scheme of the riser reactor is proposed for the first time. The experimental study on the biomass catalytic cracking for aromatics by using the riser reactor is carried out. The effects of different reaction temperatures and reaction times on the yield and selectivity of bio-aromatics are investigated. It provides a new idea for the continuous bio-aromatics production process.

2. Experimental

2.1. Materials and calculating equation
The catalyst used in these experiments was chosen on the basis of a previous study, was Zn²⁺ exchanged zeolite type catalyst supplied by China University of Petroleum. The specific surface area of the catalyst was over 350m²/g, pore volume is over 0.6mL/g, bulk density is around 1250kg/m³, average particle size is 110~140μm, abrasiveness index is less than 2.7%h¹. Prior to all reactions, the catalyst was fluidized calcined in the reactor at 650°C for 7h.

In this study, corn stalk was used as the feedstock. Before the experiment, the corn stalk is carried into pretreatment unit, the feedstock is obtained by multi-stage pulverizing and drying. The drying process was composed of rotary dryer, the operating temperature was 105°C. The average particle size required for feeding was 160-200μm. The feedstock properties are shown in Table 1.

Table 1. Components analysis of corn stalk feedstock

| Proximate analysis [% (ad)] | Elemental analysis [%] | Net Heating value [MJ/kg] |
|---------------------------|-------------------|-----------------|
| M    | V    | A    | Fe   | C    | H    | O    | N    | S    | |
| 8.27 | 63.76| 6.01 | 18.29| 41.21| 5.97 | 45.91| 0.78 | 0.12 | 15.67 |

Equation 1 shows the WHSV of the reaction.

\[
WHSV(h^{-1}) = \frac{\text{feedstock flow rate (kg/h)}}{\text{weight of catalyst (kg)}}
\]  

The WHSV is calculated by dividing the feedstock flow rate by the amount of catalyst reservation amount inside the riser reactor. As shown in Eq.2, the residence time of the gas was calculated by dividing the length of the riser reactor by the average gas linear velocity.
Gas residence time = \frac{\text{length of the riser reactor (m)}}{\text{average gas linear velocity (m/s)}} \quad (2)

2.2. Analytical methods and instruments

The mass of the liquid product obtained by the experiment is calculated by a balance with regard to the loss in the reaction system piping, and the mass of the gas phase product obtained from the gas-liquid separator was calculated by float flowmeter. The solid product yield is calculated by subtraction method. The biogas component was analyzed by GC102D gas chromatograph (Shanghai Analytical Instrument Company) and the volume fraction was calculated. The packed column C2000 was selected as the column, and the column temperature was 60 °C.

After the liquid product was separated by oil-water separation, the oil phase components were analyzed by Agilent GCMS5975 GC/MS analyzer. Gas chromatographic conditions: capillary column DB-1MS (inner diameter is 0.25mm), column temperature is 50°C, holding for 5 minutes, then raised to 250°C by 10°C/s. Mass spectrometry operating conditions: ionization mode is EI, bombardment energy is 70eV, scanning mass range is 30–500u, scanning rate is 1000amu/s.

2.3. Process design

The main devices of the bio-aromatics production process are riser reactor (9m), catalyst regeneration reactor, gas-solid separator and condenser, which are all made of 316L stainless steel. The feedstock enters from the lower part of the riser reactor. The catalytic cracking reaction occurs under the action of the catalyst to generate high temperature cracking gas and carbon powder. The high temperature gas and the deactivated catalyst and carbon powder pass through the fast separator and the two-stage cyclone, then the deactivated catalyst and carbon powder enter the first regenerator from the inclined tube. In the regenerator, the deactivated catalyst is calcined to remove over 98wt% of surface carbon deposition. Then the regenerated catalyst is recycled from the inclined tube into the lower part of the riser reactor. The heat required for the catalyst regeneration process is provided by the carbon powder, and the carbon powder is burned to obtain the ash product, which could be discharged with the exhaust gas from the top of the first regeneration. The high temperature gas exits the reactor and then enters the condenser to separate two phase products—biogas and liquid, a small portion of the biogas is used for rising gas, and the rest is mostly used for cogeneration or civilian fuel. The process diagram of biomass catalytic cracking to bio-aromatics is shown in Fig.1.

![Process diagram of biomass catalytic cracking to bio-aromatics](image_url)

**Figure 1.** Process of biomass catalytic cracking to bio-aromatics.
2.4. Experimental setup
The feedstock is carried into the lower part of the riser reactor with the feed carrier gas, the feeding velocity is 50kg/h. The operating pressure of the reactor is 0.25MPa, the operating temperature is 480-540°C, the average operating gas velocity is 2.5m/s, and the reaction time is 3s. The space velocity is less than 80h⁻¹, the mass flow ratio of feedstock to catalyst is 1:8, and the flow ratio of feed carrier gas to riser gas is 1:12. Under the above operating conditions, the feedstock occurs cracking and deoxidation under the action of the zeolite catalyst.

The high temperature gas and the carbon powder passes enters the rapid separator. Most of the catalyst and the carbon powder are separated from the cracking product and then enters the catalyst regenerator through the inclined tube. The operating pressure of the regenerator is 0.29MPa, the operating temperature is 650°C, the peroxidation amount is 5%, and the operation velocity of the disengager is over 0.2m/s. After the reaction product leaves the top of the riser reactor, it enters the two-stage cyclone separator, and then enters the condenser to exchange heat with the circulating water. The condenser outlet temperature is kept below 50°C, and the gas-liquid mixture enters the gas-liquid separator for separation, the operating velocity of the separator is less than 0.1m/s, then the liquid product is obtained in the bottom of the device and the biogas product is obtained in the top. A small portion of the biogas is used for rising gas.

3. Results and discussion

3.1. Optimal reaction temperature
Based on the previous research of CECEP engineer [14], four temperature points (480°C, 500°C, 520°C, 540°C) were selected for the test, other process parameters were all the same. The catalyst was pre-calcined for 6 hours, the time of feeding is 3 hours. Three phases products of ash, biogas and liquid were obtained in the experiment. The variation of the oil phase of the liquid and gas yield against the reaction temperature are shown in Fig. 2.

![Figure 2. Products distribution against reaction temperature.](image)

From Fig.2, within the temperature range, the high yield of oil phase in the liquid product is 19.87wt%, obtained at 500°C, while gas yield is 33.5wt%. It can be seen from the trend of the curve in the Fig.2 that the yield of the oil phase product reaches a point of extreme value, and the downward trend is stronger than that of the solid product. Via analysis, it is considered that along with the increasing of the temperature, the gasification reaction gradually dominates the catalytic cracking process, which is not conducive to oil phase production. Therefore, the parameters of the maximum yield of oil phase product are selected as the optimal reaction conditions.
3.2. Property Analysis of oil phase product
Properties of the oil phase obtained under the optimal reaction condition is analyzed, the data is shown in Table 2. According to the analysis result, bio-aromatics yield in the oil phase is about 78wt%, the value converted to the feedstock is about 15.5wt%.

Table 2. Property analysis of oil phase product

| Oil phase properties | Elemental analysis [%] |
|----------------------|------------------------|
| Density [g/ml]       | Kinematic viscosity [mm²/g] | Net heating value [MJ/kg] | C       | H       | O       | N       | S       |
| 8.27                 | 63.76                  | 37.5                  | 87      | 6.1     | 6.7     | 0.2     | trace   |

According to the Table 3, bio-aromatics yield in the oil phase is about 78wt%, the main components are benzene, toluene, xylene, naphthalene, trimethyl-benzene and indene, they could be separated by aromatics extraction process.

Table 3. Main composition analysis of oil phase product

| Benzene [wt%] | Toluene [wt%] | Xylene [wt%] | Naphthalenes [wt%] | Trimethylbenzene [wt%] | Indenes [wt%] | Furan and phenols [wt%] |
|---------------|---------------|--------------|--------------------|------------------------|---------------|-------------------------|
| 6.2           | 7.1           | 11.5         | 44.0               | 4.2                    | 5.0           | 7.0                     |

3.3. Property Analysis of biogas product
Properties and main composition of the biogas obtained under optimal reaction condition is analyzed, the data is shown in Table 4 and Table 5.

Table 4. Property Analysis of biogas product (273.15K, 0.1MPa)

| Density [kg/m³] | Net heating value [MJ/m³] | Gas viscosity [Pa-sec] | Heat Capacity [J/kg-K] | average molecular weight |
|-----------------|---------------------------|------------------------|------------------------|-------------------------|
| 1.39            | 13.66                     | 1.35E-05               | 1116.87                | 31.41                   |

Table 5. Main composition analysis of biogas [vol%]

| H₂      | C₂H₆ | C₂H₄ | CH₄  | CO    | C₃H₆ | C₃H₈ | l-C₄H₈ | C₄H₁₀ | CO₂   |
|---------|------|------|------|-------|------|------|--------|-------|-------|
| 13.27   | 3.04 | 2.1  | 9.85 | 20.16 | 3.59 | 2.52 | 0.24   | 0.15  | 45.03 |

The biogas could be used for rising gas, and as material for hydrogen production, according to calculation, it is estimated that 12t biogas could product 1t H₂ through dry reforming transformation and PSA process.

4. Conclusions
This paper mainly provides a new efficient and easily scaled method for bio-aromatics production, and use this continual reaction-regeneration system to operate the biomass catalytic cracking process, according to the process research, the influence rule of reaction temperature against bio-aromatics yield is similar with biomass fast pyrolysis process.

The riser reaction type of biomass catalytic cracking process could be settled the problem of traditional fixed-bed, bubbling fluidized-bed and etc. that lack of deactivated catalyst continual regenerating process, which is beneficial for continual production, and settled the problem that electric heating cannot supply the heat absorbed by the catalytic cracking reaction in time, the required reaction heat is supplied by regenerated catalyst. The whole process is efficient and environmental-
friendly, that could be available to industrial pilot plant design studies, it is estimated that the bio-aromatics yield would be furthermore promoted by the amelioration of zeolite catalyst and scaled-up process.

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