# Catalytic Fast Pyrolysis of Biomass in a Fluidized Bed with Fresh and Spent Fluidized Catalytic Cracking (FCC) Catalysts

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# Catalytic Fast Pyrolysis of Biomass in a Fluidized Bed with Fresh and Spent Fluidized Catalytic Cracking (FCC) Catalysts

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The conversion of biomass into bio-oil using fast pyrolysis technology is one of the most promising alternatives to convert biomass into liquid products. However, substituting bio-oil for conventional petroleum fuels directly may be problematic because of the high viscosity, high oxygen content, and strong thermal instability of bio-oil. The focus of the current research is decreasing the oxygen and polymerization precursor content of the obtained bio-oil to improve its thermal stability and heating value. Catalytic fast pyrolysis of corncob with different percentages (5, 10, 20, and 30% by volume) of fresh fluidized catalytic cracking (FCC) catalyst (FC) and spent FCC catalyst (SC) in bed materials was conducted in a fluidized bed. The effects of the catalysts on the pyrolysis product yields and chemical composition of the bio-oil were investigated. A greater catalyst percentage lead to a lower bio-oil yield, while a lower catalyst percentage lead to little change of the composition of the bio-oil. The best percentages of FC and SC were 10 and 20%, respectively. FC showed more catalytic activation in converting oxygen into CO, $CO_2$, and $H_2O$ than SC, but the oil fraction yield with FC was remarkably lower than that with SC because of more coke formation. The gas chromatography/mass spectrometry (GC/MS) analysis of the collected liquid in the second condenser showed that the most likely polymerization precursors, such as 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 4-ethyl-2-methoxy-phenol, 2-methoxy-4-vinylphenol, and 2,6-dimethoxy-phenol decreased, while monofunctional phenols, ketones, and furans increased compared to that in the noncatalytic experiment. The hydrocarbons increased with the increase of the catalyst percentages, and this contributed to the decrease of the oxygen content of the bio-oil. Multi-stage condensation achieved a good separation of the oil fraction and water.

## Introduction

Environmental issues and the security of energy supplies, especially petroleum resources, have stimulated the interest in the development of alternatives for fossil-based energy carriers and chemicals. Plant biomass is the only current sustainable source that could be converted into liquid fuels.[1,2] In comparison to petroleum resources, the applications of the liquid fuels converted from biomass are a $CO_2$-neutral process considering the global carbon balance. Biomass fast pyrolysis can produce considerable liquid fuel, named as bio-oil. Many studies have focus on the production of bio-oils using fast pyrolysis technology in different pyrolysis reactors,[3−7] and a bio-oil yield of up to 75% was reported.[8] Although bio-oils produced by fast pyrolysis are very promising technology, there are still many obstacles that need to be overcome before they can be used as transport oil. Crude bio-oils are not soluble with petroleum-derived fuels. They contain more than 400 components, including acids, ketones, aldehydes, alcohols, esters, phenols, and aromatic derivatives. Bio-oils can polymerize with time, and this process can be accelerated at high temperatures and an oxygen-exposure environment. The main problems of burning bio-oils include difficult ignition because of high oxygen content and high water content, corrosiveness because of high acid content, and coking caused by the polymerization of thermally unstable compounds. These problems have limited the applications of bio-oils. To reach the fuel usual standard specifications, the bio-oil needs to be upgraded. The heating value and thermal instability of the bio-oil should be improved, and the acid content should be decreased.

The recent upgrading techniques of bio-oil mainly include hydrodeoxygenation, emulsification, and catalytic cracking. The hydrodeoxygenation process is performed in hydrogen providing solvents under pressurized conditions of $H_2$ with Co−Mo/$Al_2O_3$, Ni−Mo/$Al_2O_3$, or Ni−W/$Al_2O_3$ catalysts.[9,10] Oxygen is removed as $H_2O$ and $CO_2$, and correspondingly, the energy density is elevated. This process needs complicated equipment, superior techniques, and excess cost and usually is halted by catalyst deactivation and reactor clogging.[11]

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Bio-oils can be emulsified with a surfactant.[12–14] Although emulsification does not demand redundant chemical transformations, the high cost and energy consumption cannot be neglected. Besides, the accompanying corrosion to the engine is inevitably serious.[11] In the technology of catalytic cracking, the vapors of bio-oils are upgraded in a static atmosphere with acidic catalysts (HZSM-5, $Al_2O_3$, Al-MCM-41, etc.).[15–17] Oxygen is removed as $H_2O$, $CO_2$, and CO. Catalytic cracking technology offers a cheaper route to convert oxygenated components into hydrocarbons. However, catalytic cracking reactions usually lead to high coking and a remarkable decrease of oil fraction yield. The search for a cheap and low-coking catalyst for bio-oil upgrading is the aim of many research activities.[18] A fluidized catalytic cracking (FCC) catalyst, used in a commercial fluid catalytic cracking unit, was applied to polyethylene and biomass catalytic pyrolysis by some researchers recently. Lee et al.[19,20] used a spent FCC catalyst (SC) in catalytic pyrolysis of polyethylene and found that the SC was a very promising catalyst to convert heavy molecular-weight vapors into the gasoline range of molecular-weight vapors. Lappas et al.[21] studied catalytic fast pyrolysis of lignocell in a circulating fluidized-bed (CFB) reactor using the FCC catalyst as an additive. Corma et al.[22] investigated catalytic cracking reaction pathways and the role of several catalysts, including a fresh FCC catalyst (FC), an equilibrium FCC catalyst with metal impurities, using glycerol and sorbitol as the representatives of biomass-derived oxygenates. Ioannidou et al.[23] reported the results of noncatalytic and catalytic pyrolysis of corn stalks in a fixed-bed reactor. Adam et al.[18] compared seven mesoporous catalysts (four Al-MCM-41-type catalysts, an equilibrium FCC catalyst, and two SBA-15-type catalysts) and how they can convert the pyrolysis vapors of spruce wood in a fixed bed. They found that the equilibrium FCC catalyst produced more promising products.

In this work, a novel process of *in situ* catalytic fast pyrolysis of biomass in a fluidized-bed reactor was proposed. This proposed system is a 2-in-1 process, which integrates fast pyrolysis bio-oil production with catalytic bio-oil upgrading using a catalyst into one chamber. This proposed process is a promising alternative because of its much encouraging economics by the elimination of the costly condensation/re-evaporation processes required for bio-oil upgrading proces-

**Table 1. Main Characteristics of the Corncob (Air-Dry Basis)**

| proximate analysis (wt %) | | | | LHV (MJ/kg) | ultimate analysis (wt %) | | | |
|---|---|---|---|---|---|---|---|---|
| FC | V | A | M | $Q_{net}$ (MJ/kg) | C | H | $O^a$ | N |
| 17.15 | 71.80 | 2.41 | 8.64 | 16.19 | 39.76 | 5.15 | 43.68 | 0.30 |

$^a$ By difference.

**Table 2. Characteristics of FC and SC**

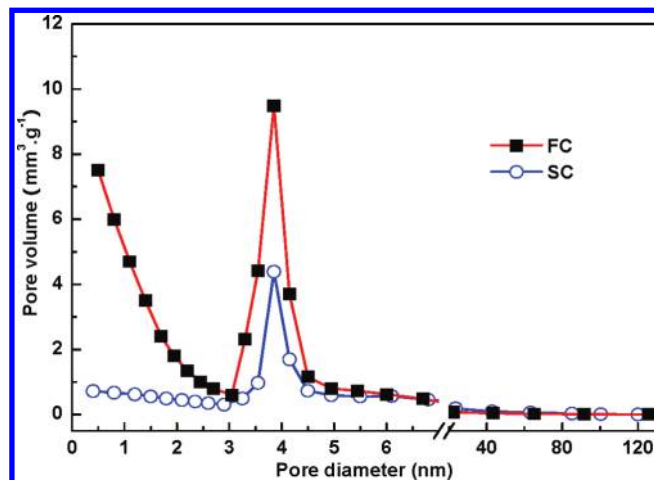| sample | FC | SC |
|---|---|---|
| BET surface area ($m^2$/g) | 242.65 | 100.65 |
| total pore volume ($cm^3$/g) | 0.21 | 0.16 |
| average pore width (nm) | 3.44 | 6.27 |
| average pore diameter (nm) | 4.85 | 9.28 |



**Figure 1.** Pore distributions of FC and SC.

sing. Besides, the *in situ* catalytic fast pyrolysis could produce more upgrading bio-oil than that bio-oil offline upgrading process because of less thermal cracking (leading to more char and coke yield). The experiments of biomass catalytic fast pyrolysis were conducted in the reactor with a FC and SC. The effects of different catalyst percentages (5, 10, 20, and 30% by volume) in bed materials on the pyrolysis product yields and oil fraction chemical composition were studied. The multi-stage condensation was used to collect the heavy oil fraction, light oil fraction, and aqueous-phase fraction. The coke and oil fraction yields of tests with FC and SC were compared to each other, and the possible reasons were analyzed from their properties.

## Experimental Section

**Biomass.** Corncob used in this study was collected from the city of Linyi in the Shandong Province, China. Prior to all experiments, the corncob was ground in a high-speed rotary cutting mill and sieved to 1.0−2.0 mm in particle sizes. Then, the particles were dried at 80 °C until a constant weight. Table 1 shows the characteristics of the corncob.

**Catalyst.** Both FC and SC used in this study were supplied by Sinopec Yangzi Petrochemical Company, Ltd. SC was recovered from a conventional FCC unit. Actually, it is a deactivated catalyst for the crude oil catalytic cracking process, but it still has high activity for biomass conversation. The particle sizes of the catalysts distributed between 0.05 and 0.3 mm, and the larger particle size of them (0.2−0.3 mm) was sieved out. The selected catalysts were dried at 120 °C for 2 h to remove moisture and kept in a desiccator for experiments. The characteristics and pore distribution of the catalysts are shown in Table 2 and Figure 1, respectively. The composition of SC was analyzed

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**Table 3. Chemical Composition of SC**

| composition | percentage (%) |
|---|---|
| $Al_2O_3$ | 49.58 |
| $SiO_2$ | 39.71 |
| $La_2O_3$ | 2.03 |
| $P_2O_5$ | 1.46 |
| CaO | 1.10 |
| $CeO_2$ | 0.99 |
| $Fe_2O_3$ | 0.66 |
| NiO | 0.62 |
| $TiO_2$ | 0.24 |
| ZnO | 0.23 |
| $K_2O$ | 0.19 |
| $V_2O_5$ | 0.17 |
| $Na_2O$ | 0.14 |
| $Sb_2O_3$ | 0.14 |
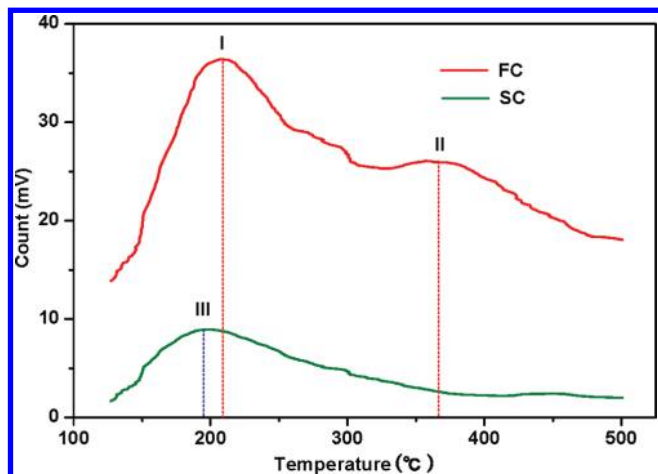


**Figure 2.** $NH_3$−TPD curves of FC and SC.

using an X-ray fluorescence (XRF) spectrometer, and the results are listed in Table 3. $NH_3$−temperature-programmed desorption (TPD) was applied to determine the acid sites of the catalysts, and the curves are shown in Figure 2.

**Experimental Setup.** A schematic diagram of the pyrolysis system used in this study is shown in Figure 3. The pyrolysis system was described elsewhere,[24] consisting of a gas preheater, the fluidized-bed reactor (length, 400 mm; internal diameter, 30 mm), condensers, filters, accumulative flowmeter, and gas-collecting bag. A porous plate and two pieces of wire netting (200-mesh size) at the bottom of the reactor were used to support bed materials and provide a uniform distribution of the fluidizing gas. The reactor used quartz sand with a particle size of 0.15−0.25 mm or its mixture with the catalyst as bed materials and pure nitrogen (99.999%) as the fluidizing gas. The flow rate of $N_2$ was controlled by a rotameter, and the volume of product gas was measured by an accumulative flowmeter. Before entering the reactor, $N_2$ was heated to about 400 °C by a preheater. A cylindrical furnace was used to supply the heat needed in the pyrolysis reactions. The connecting pipe between the reactor and condensers was maintained at 400 °C to prevent tar condensation by a strip heater. A ceramic filter was installed after the reactor to remove fine particles. After the ceramic filter, the product vapors were introduced to three condensers in turn. The first, second, and third condensers were operated at 100, 45, and 0 °C to obtain the heavy oil fraction, light oil fraction, and aqueous-phase fraction, respectively. Cotton and silica gel filters were used to ensure all of the condensable vapors were captured. The noncondensable gas was collected by a bag for analysis.

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**Procedure and Product Collection.** At the beginning of each test, sand or its mixtures with different catalyst percentages (5, 10, 20, and 30% by volume) were placed in the reactor and 6 g of corncob was placed in the feed hopper purged with $N_2$ to guarantee an inert atmosphere during the experiment. The furnace started to heat the reactor. After the desired temperature in the reactor was attained, the feedstock was added to the bed. Liquid products were collected by three condensers, and noncondensable gas was collected using a gas-collecting bag. The experiment was carried out for approximately 10 min to ensure complete pyrolysis of the corncob. After the experiment, the furnace was turned off and the $N_2$ was maintained until the reactor reached room temperature to avoid the oxidation of char. The char was separated from bed materials and weighted. The condensers were cleaned using ethanol, and the washings were heated at 60 °C for ethanol evaporation. The total liquid products include the collecting liquids by the three condensers, weight increases of the cotton wool and silica gel filters, and the weight of the evaporation residue washings. The bed materials were dried at 120 °C until a constant weight and then combusted in a muffle furnace at 600 °C for 2 h. The coke output was determined by the weight loss of bed materials before and after being combusted. The gas output was calculated by the total collected gas volume measured by the accumulative flowmeter and the components, and their percentages were determined by gas chromatography (GC) analysis. The product yields were calculated from the weights of products divided by the feedstock weight (air-dry basis).

Each experiment was repeated 3 times under the same conditions, and the mass balance in all of the experiments was in the range of 92−98%.

**Product Analysis.** The noncondensable gas composition was detected using a GC 9890A (Shanghai Linghua Co., Ltd., China). The water contents of the collected liquids were determined using a method of Karl Fischer titration. A Vario EL III (Elementar Company, Germany) instrument was used to analyze the elemental composition of the collected liquids.

GC/mass spectrometry (MS) analysis of the liquid yield was performed using an Agilent 7890A-5975C. High-purity helium was used as the carried gas at a constant flow rate of 1.0 mL/min. The GC separation was carried out on a fused silica capillary column named VF-5 ms (30 m × 0.25 mm × 0.25 $\mu$m). A split of the carrier gas (1:30) was used. The temperature of the GC/MS injector was held at 280 °C. The injection volume was 1 $\mu$L. The GC oven temperature was programmed from 40 to 180 °C at 5 °C/min and then to 280 °C at 10 °C/min. It was applied with an isotherm period of 3 min at 50 °C, 2 min at 180 °C, and 2 min at 280 °C. Typical operating conditions were an ionization energy of 70 eV and scan per second over the electron range of ($m/z$) 40−550 amu.

## Results and Discussion

**Product Yields.** Experimental tests with and without catalyst percentages of 5, 10, 20, and 30% in bed materials were investigated in this work. All of the tests were conducted in a static atmosphere with a pyrolysis temperature of 550 °C, fluidizing gas flow rate of 1.5 L/min, bed height of 10 cm, and biomass particle size of 1.0−2.0 mm. The fluidized bed was operated at a bubbling bed regime. The fluidizing gas velocity is 4.2 times the minimum fluidization gas velocity at the reaction temperature. The dependences of product yields on FC and SC percentages are shown in Figures 4 and 5, respectively.

As illustrated in Figure 4, the total liquid yield of 54.6% was obtained in the noncatalytic experiment, including 32.4% of the oil fraction yield and 22.2% of the water yield. With the increase of the catalyst percentage from 0 to 30%, the oil fraction yield decreased monotonously to 11.8% with FC and to 18.1% with SC, while the water yield increased to about 27% with either of the two catalysts. Besides, the oil
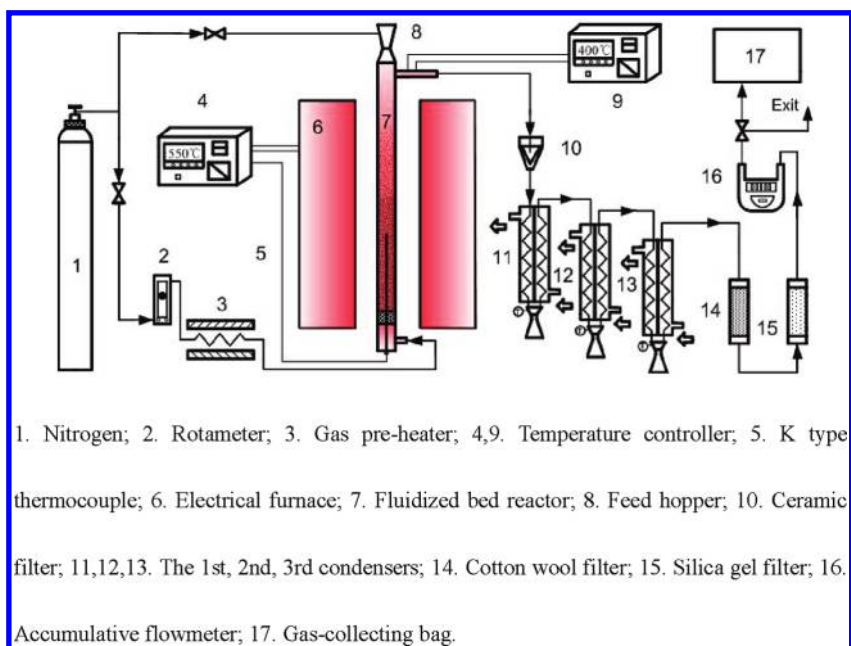
**Figure 3.** Schematic diagram of the fluidized-bed system for fast pyrolysis of biomass.
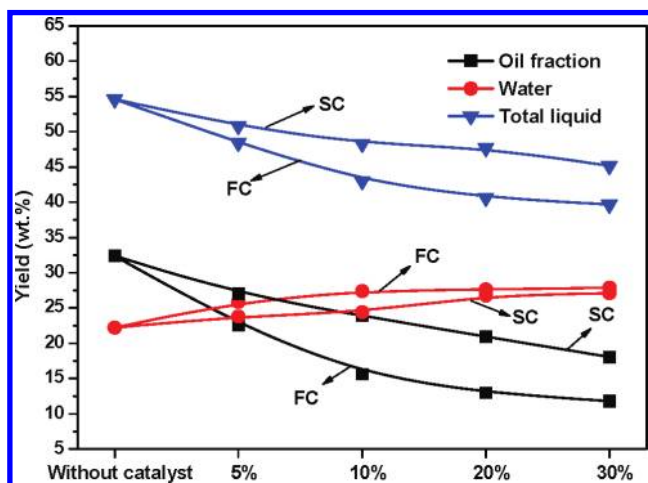


**Figure 4.** Dependences of liquid yields on FC and SC percentages in bed materials.
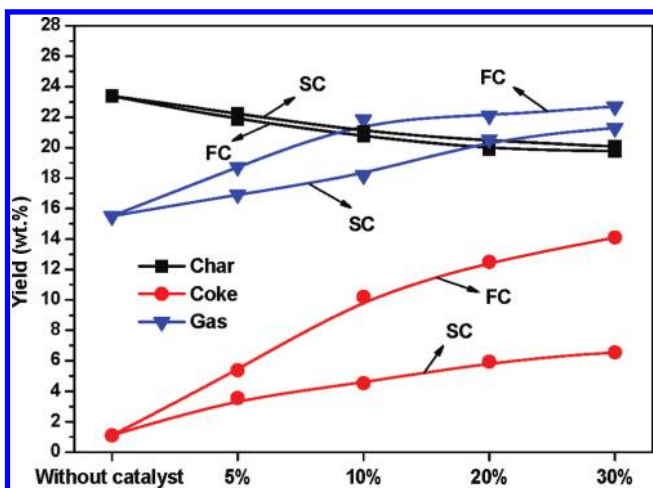


**Figure 5.** Dependences of char, coke, and gas yields on FC and SC percentages in bed materials.

**Table 4. Composition of Pyrolysis Gases (wt % on Biomass)**

| catalyst | CO | $CO_2$ | $CH_4$ | $H_2$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | total |
|---|---|---|---|---|---|---|---|---|---|
| no catalyst | 5.26 | 9.20 | 0.56 | 0.03 | 0.21 | 0.05 | 0.16 | 0.03 | 15.50 |
| 5% FC | 6.29 | 11.12 | 0.65 | 0.02 | 0.31 | 0.05 | 0.28 | 0.02 | 18.74 |
| 10% FC | 8.04 | 12.08 | 0.84 | 0.05 | 0.38 | 0.08 | 0.32 | 0.05 | 21.84 |
| 20% FC | 8.25 | 12.31 | 0.67 | 0.08 | 0.35 | 0.06 | 0.31 | 0.08 | 22.11 |
| 30% FC | 8.99 | 11.81 | 0.75 | 0.12 | 0.41 | 0.09 | 0.42 | 0.11 | 22.70 |
| 5% SC | 5.46 | 10.16 | 0.65 | 0.04 | 0.33 | 0.06 | 0.18 | 0.05 | 16.93 |
| 10% SC | 6.24 | 10.04 | 0.87 | 0.04 | 0.36 | 0.06 | 0.52 | 0.06 | 18.19 |
| 20% SC | 7.31 | 11.12 | 0.96 | 0.06 | 0.42 | 0.05 | 0.55 | 0.08 | 20.55 |
| 30% SC | 7.91 | 11.28 | 0.67 | 0.07 | 0.53 | 0.08 | 0.61 | 0.15 | 21.30 |
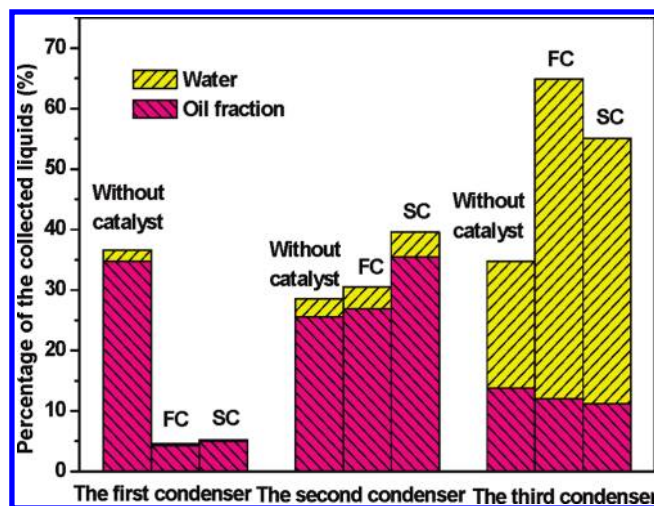


**Figure 6.** Distributions of liquid products collected by the three condensers in the noncatalytic test and catalytic tests with FC and SC.

fraction yield with FC was lower than that with SC at the same catalyst percentages, while the water yield showed an opposite situation.

It can be seen from Figure 5 that the gas yield increased monotonously from 15.5 to 22.7% with FC and to 21.3% with SC as the catalyst percentage increased from 0 to 30%. The
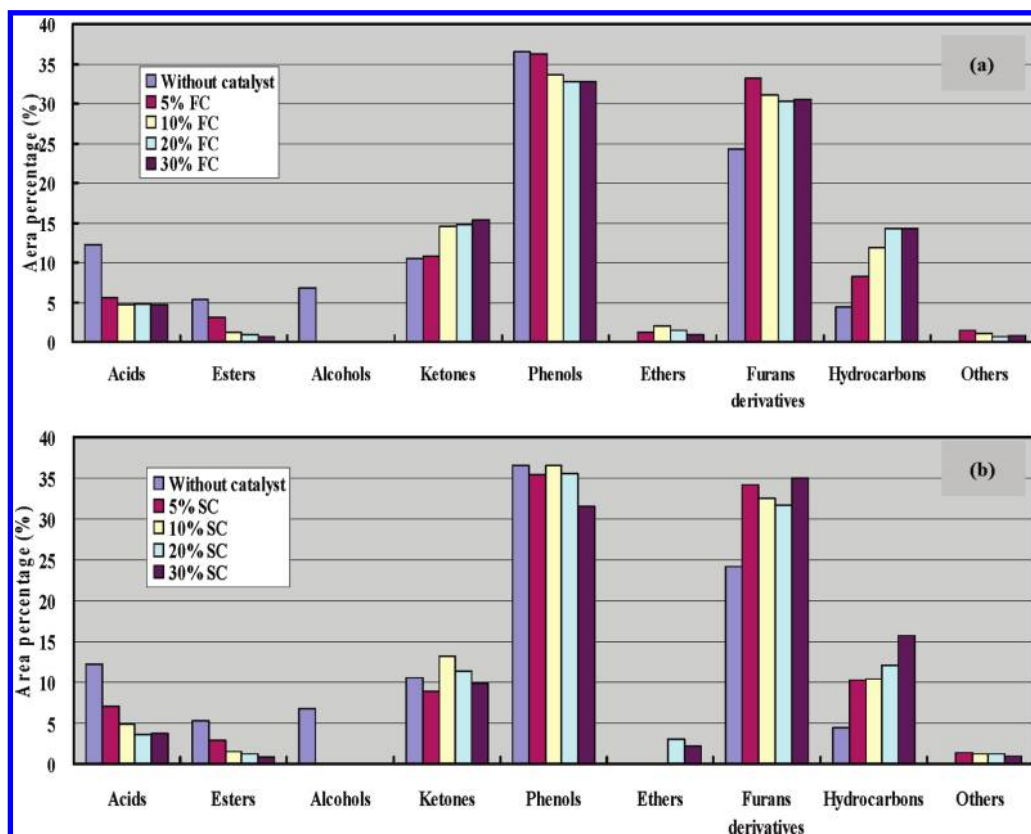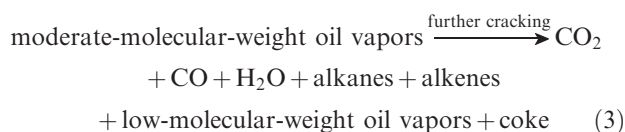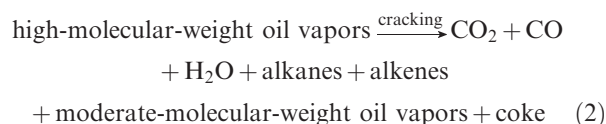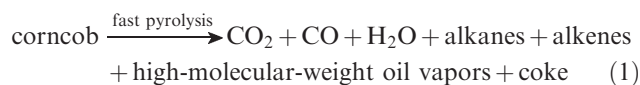
**Figure 7.** Area percentages of different chemical groups of the liquid products collected by the second condenser in noncatalytic and catalytic tests with different percentages of (a) FC and (b) SC.

char yield decreased from 23.4% without catalyst to about 20% at the catalyst percentage of 30% with either of the two catalysts. The use of the catalysts led to a noticeable increase of coke yields, which increased from 1.1 to 14.1% with FC and to 6.6% with SC. The coke and gas yields in catalytic tests with FC were higher than those with SC at the same catalyst percentages. Ioannidou et al.,[23] who studied corncob fast pyrolysis with a FCC catalyst in a fixed bed, obtained a lower oil fraction (about 10%) and gas yield (12.3%) and a much higher char yield (33.0%) than our study.

Table 4 lists the yields of gas components in noncatalytic and catalytic tests. As shown in the table, the main components in the pyrolysis gas were CO and $CO_2$. In addition, the main hydrocarbon products were alkanes and alkenes. Their yields increased with the increase of the catalyst percentage.

The total reactions in fast and catalytic pyrolysis are listed below.

$$\text{corncob} \xrightarrow{\text{fast pyrolysis}} CO_2 + CO + H_2O + \text{alkanes} + \text{alkenes}$$
$$+ \text{high-molecular-weight oil vapors} + \text{coke} \quad (1)$$

$$\text{high-molecular-weight oil vapors} \xrightarrow{\text{cracking}} CO_2 + CO$$
$$+ H_2O + \text{alkanes} + \text{alkenes}$$
$$+ \text{moderate-molecular-weight oil vapors} + \text{coke} \quad (2)$$

$$\text{moderate-molecular-weight oil vapors} \xrightarrow{\text{further cracking}} CO_2$$
$$+ CO + H_2O + \text{alkanes} + \text{alkenes}$$
$$+ \text{low-molecular-weight oil vapors} + \text{coke} \quad (3)$$

The addition of the catalyst decreased the oil fraction yield mainly because of reactions 2 and 3. The two reactions con-

verted higher molecular-weight oil vapors into smaller ones, with water, gas, and coke as byproducts. Therefore, the water, gas, and coke yields increased after using the catalysts. The $NH_3$−TPD analysis of the catalysts (see Figure 2) shows that FC had a higher number of strong acid sites than SC. These strong acid sites favored reaction 3, and more moderate-molecular-weight oil vapors in catalytic tests with FC underwent further cracking and produced more water, gas, and coke. Therefore, as shown in Figures 4 and 5, the oil fraction yield with FC was lower than that with SC at the same catalyst percentages, while the water, gas, and especially, coke yields with FC were higher than those with SC. A similar conclusion has been obtained by Iliopoulou et al., who carried out wood pyrolysis experiments with different Al-MCM-41-type catalysts in a fixed-bed reactor.[25] Figure 1 displays the pore volume distribution in conjunction with the pore diameter. From the figure, we can conclude that the total volume of micropores of FC is distinctly higher than that of SC. The micropores offered the place for further cracking (reaction 3). The moderate-molecular-weight oil vapors obtained from reaction 2 would undergo further cracking in the micropores with the strong acid sites of FC. This process also led to a decrease of the oil fraction yield and an increase of the water, gas, and coke yields. The transition-metal content in SC (see Table 3) might affect the distribution of products. However, their contribution in the case of the SC is expected to be minimal compared to the main catalytic effect of SC because of their small concentrations.[18] As for the decrease of the char yield with catalyst, it can be attributed to further pyrolysis of char precursors on the surface of the catalyst.

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**Table 5. Chemical Composition of the Collected Liquid by the Second Condenser**

| peak | retention time (min) | compound | formula | $M_w$ | without catalyst | 5% FC | 10% FC | 20% FC | 30% FC | 5% SC | 10% SC | 20% SC | 30% SC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2.22 | methyl vinyl ketone | $C_4H_6O$ | 70 | | | 0.72 | 0.84 | 0.83 | | 0.67 | 0.81 | 0.85 |
| 2 | 3.02 | benzene | $C_6H_6$ | 78 | 0.63 | | | | | | | | |
| 3 | 3.11 | acetic acid | $C_2H_4O_2$ | 60 | 11.75 | 5.65 | 4.62 | 4.77 | 4.70 | 7.02 | 4.79 | 3.57 | 3.74 |
| 4 | 4.09 | toluene | $C_7H_8$ | 92 | 2.54 | 5.07 | 7.63 | 8.13 | 8.28 | 4.29 | 4.60 | 6.48 | 7.61 |
| 5 | 4.32 | 1-butene, 2,3-dimethyl | $C_6H_{12}$ | 84 | 1.21 | 3.06 | 3.96 | 4.39 | 3.80 | 5.80 | 5.42 | 5.32 | 6.27 |
| 6 | 4.91 | 1-hydroxy-2-butanone | $C_4H_8O_2$ | 88 | 3.48 | | 0.92 | 0.83 | 0.43 | 2.28 | 2.29 | 0.93 | 0.55 |
| 7 | 6.00 | butanoic acid, 2-oxo | $C_4H_6O_3$ | 102 | 0.52 | | | | | | | | |
| 8 | 6.18 | propane, 1,1-diethoxy | $C_7H_{16}O_2$ | 132 | | 1.14 | 1.96 | 1.47 | 0.89 | | | 3.05 | 2.23 |
| 9 | 6.47 | 2-ethoxytetrahydrofuran | $C_6H_{12}O_2$ | 116 | 0.76 | 0.76 | 0.91 | 1.24 | 1.08 | 0.84 | 0.89 | 1.24 | 1.43 |
| 10 | 6.71 | furfural | $C_5H_4O_2$ | 96 | 8.79 | 9.60 | 8.65 | 8.58 | 8.42 | 8.94 | 8.73 | 8.93 | 9.58 |
| 12 | 7.44 | 2-furanmethanol | $C_5H_6O_2$ | 98 | 0.88 | | | | | 0.38 | 1.27 | 1.12 | 1.53 |
| 13 | 7.82 | *p*-xylene | $C_8H_{10}$ | 106 | | | 1.48 | 1.58 | | | | | 1.37 |
| 14 | 7.87 | 2-propanone, 1-(acetyloxy) | $C_5H_8O_3$ | 116 | 5.29 | 3.02 | 1.22 | 1.00 | 0.67 | 2.85 | 1.46 | 1.24 | 0.89 |
| 15 | 9.26 | 2(5*H*)-furanone | $C_4H_4O_2$ | 84 | | 1.33 | 2.21 | 2.80 | 3.01 | 1.37 | 2.96 | 2.15 | 1.74 |
| 16 | 9.28 | cyclohexanol, 2,3-dimethyl | $C_8H_{16}O$ | 128 | 0.36 | | | | | | | | |
| 17 | 9.62 | 1,2-cyclopentanedione | $C_5H_6O_2$ | 98 | | 2.96 | 3.61 | 3.24 | 2.81 | 3.01 | 4.58 | 4.26 | 3.85 |
| 19 | 10.98 | 2-cyclopenten-1-one, 3-methyl | $C_6H_8O$ | 96 | | 5.08 | 5.65 | 6.86 | 6.81 | 1.21 | 1.32 | 1.60 | 1.68 |
| 20 | 11.21 | cyclohexanol, 4-methyl | $C_7H_{14}O$ | 114 | 3.02 | | | | | | | | |
| 21 | 11.52 | phenol | $C_6H_6O$ | 94 | 6.49 | 8.44 | 12.16 | 14.96 | 15.86 | 5.78 | 6.67 | 9.90 | 10.57 |
| 22 | 12.00 | oxazolidine, 2,2-diethyl-3-methyl | $C_8H_{17}NO$ | 143 | | 1.48 | 1.05 | 0.64 | 0.82 | 1.37 | 1.20 | 1.27 | 0.91 |
| 23 | 12.61 | furan, 2,5-diethoxytetrahydro | $C_8H_{16}O_3$ | 160 | 3.69 | 13.34 | 17.26 | 17.64 | 18.08 | 12.52 | 12.35 | 16.13 | 19.00 |
| 24 | 12.95 | 1,2-cyclopentanedione, 3-methyl | $C_6H_8O_2$ | 112 | | 1.83 | 2.90 | 2.47 | 3.69 | 1.86 | 3.64 | 3.24 | 2.32 |
| 25 | 13.30 | indene | $C_9H_8$ | 116 | | 0.17 | 0.22 | 0.30 | 0.58 | 0.25 | 0.34 | 0.33 | 0.51 |
| 26 | 13.50 | 2-cyclopenten-1-one, 2-hydroxy-3-methyl | $C_6H_8O_2$ | 112 | 5.07 | | | | | | | | |
| 27 | 13.84 | phenol, 2-methyl | $C_7H_8O$ | 108 | 2.78 | 2.37 | 3.79 | 4.90 | 5.05 | 2.49 | 2.72 | 3.46 | 3.63 |
| 28 | 14.47 | phenol, 4-methyl | $C_7H_8O$ | 108 | 4.77 | 5.93 | 6.61 | 7.15 | 7.86 | 5.72 | 8.72 | 8.46 | 8.01 |
| 29 | 14.90 | phenol, 2-methoxy | $C_7H_8O_2$ | 124 | 5.98 | 2.97 | 1.20 | 1.08 | 0.49 | 3.58 | 2.64 | 1.66 | 1.13 |
| 30 | 15.81 | 2-cyclopenten-1-one, 3-ethyl-2-hydroxy | $C_7H_{10}O_2$ | 126 | | 0.98 | 0.77 | 0.57 | 0.73 | 0.48 | 0.70 | 0.61 | 0.65 |
| 31 | 16.69 | phenol, 2,4-dimethyl | $C_8H_{10}O$ | 122 | 1.66 | 0.78 | 1.12 | 1.31 | 1.17 | 0.94 | 0.87 | 1.09 | 0.77 |
| 32 | 17.01 | 2-pentanone, 5,5-diethoxy | $C_9H_{18}O_3$ | 174 | 0.97 | | | | | | | | |
| 33 | 17.24 | phenol, 4-ethyl | $C_8H_{10}O$ | 122 | 3.55 | 3.41 | 2.57 | 2.35 | 1.76 | 3.59 | 3.11 | 2.50 | 2.21 |
| 34 | 17.99 | 4-s-butoxy-2-butanone | $C_8H_{16}O_2$ | 144 | 1.02 | | | | | | | | |
| 35 | 18.03 | phenol, 2-methoxy-4-methyl | $C_8H_{10}O_2$ | 138 | 1.17 | 0.71 | 0.41 | 0.44 | 0.29 | 0.89 | 0.53 | 0.46 | 0.42 |
| 36 | 18.75 | benzofuran, 2,3-dihydro | $C_8H_8O$ | 120 | 10.97 | 7.33 | 2.08 | | | 10.14 | 6.25 | 2.16 | 1.76 |
| 37 | 20.12 | 1,2-benzenediol, 3-methyl | $C_7H_8O_2$ | 124 | | 2.08 | 1.72 | | | 1.43 | 2.19 | 2.05 | 1.38 |
| 38 | 20.37 | 4-nonanol, 4-methyl | $C_{10}H_{22}O$ | 158 | 3.39 | | | | | | | | |
| 39 | 20.49 | phenol, 4-ethyl-2-methoxy | $C_9H_{12}O_2$ | 152 | 2.07 | 1.51 | | | | 2.34 | 1.45 | 0.38 | |
| 40 | 20.79 | 1,2-benzenediol, 4-methyl | $C_7H_8O_2$ | 124 | | | 0.28 | | | 0.82 | | 0.45 | |
| 41 | 21.45 | 2-methoxy-4-vinylphenol | $C_9H_{10}O_2$ | 150 | 5.20 | 2.12 | 0.56 | | | 3.69 | 2.07 | 1.00 | 0.60 |
| 42 | 22.45 | phenol, 2,6-dimethoxy | $C_8H_{10}O_3$ | 154 | 2.87 | 1.81 | 0.98 | 0.56 | 0.31 | 1.59 | 1.55 | 1.01 | 1.00 |
| 43 | 23.28 | 1,3-benzenediol, 4-ethyl | $C_8H_{10}O_2$ | 138 | | 4.19 | 2.26 | | | 2.53 | 4.02 | 3.14 | 1.81 |

**Distribution of Liquid Products in the Multi-stage Condensation Units.** In this work, three condensers were operated at different temperatures to collect the heavy oil fraction, light oil fraction, and aqueous-phase fraction, respectively. The distribution of the collected liquids (in terms of the total collected liquids by the three condensers) with 10% FC and 20% SC are shown in Figure 6. As can be seen from the figure, the application of the multi-stage condensation achieved a good separation of the oil fraction and water. The water content of the liquids collected by the first, second, and third condensers were 5.1, 10.5, and 60.3% in the noncatalytic test, while about 5−6, 10−12, and 79−82% in the presence of 10% FC or 20% SC.

As illustrated in Figure 6, the total amount of liquids collected by the first condenser decreased from 31.4% without catalyst to about 4−5% with either of FC or SC. The results indicated that the use of the catalyst brought an almost complete cracking of the heavy oil fraction. As for the second condenser, it can be seen that most of the oil fraction in the catalytic experiments (accounting for 62.2% with FC and 68.7% with SC) was collected by this condenser. The liquid collected percentages of 34.8 and 55−65% were

obtained in the third condenser in the noncatalytic and catalytic fast pyrolysis experiments, respectively. However, the collected liquids in the third condenser had little value because of their large water contents.

**Chemical Composition of the Collected Liquid in the Second Condenser.** The liquids in the first and third condensers had little value because of large amount of tar or water content inside and the most valuable oil (light oil) was in the second condenser. Figure 7 and Table 5 show the chemical groups and chemical composition of the collected liquids in the second condenser, respectively. As shown in panels a and b of Figure 7, ketones, phenols, and furan derivatives were the dominating groups of the compounds. A similar result has been reported by Adam et al.,[18] who investigated miscanthus and spruce fast pyrolysis with the FCC catalyst in a fixed bed. Acids, esters, and phenols decreased with the increase of the percentage of the catalyst, while ketones, furan derivatives, and hydrocarbons increased. Acetic acid is the main component of the acid group, and its peak area percentage decreased with the use of FCC catalysts. However, additional experiments without multi-stage condensation showed that the use of the FCC catalyst lead to a little increase of the total

**Table 6. Properties of the Collected Liquids (Dry Basis, wt %)**

| catalyst percentages | C | H | N | O[a] | HHV (MJ/kg) | PH | specific gravity |
|---|---|---|---|---|---|---|---|
| no catalyst | 52.36 | 6.82 | 0.74 | 40.08 | 19.92 | 2.90 | 1.13 |
| 10% FC | 73.12 | 9.02 | 1.85 | 16.01 | 34.24 | 5.10 | 0.95 |
| 20% SC | 71.91 | 8.94 | 1.57 | 17.58 | 32.67 | 4.90 | 0.98 |

[a] By difference.
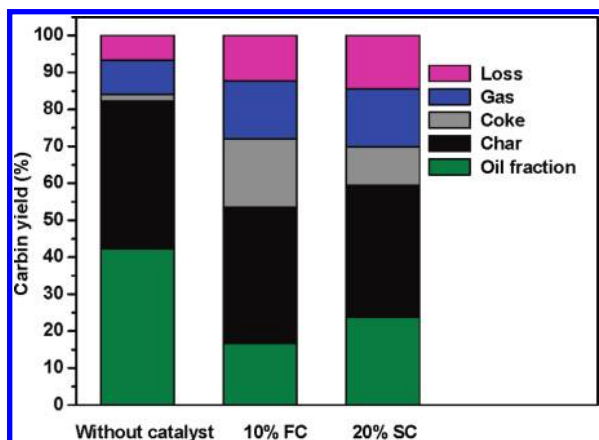


**Figure 8.** Carbon yields for the feedstocks of catalytic and non-catalytic experiments.



**Figure 9.** Oxygen yields for the feedstocks of catalytic and non-catalytic experiments.

acetic acid yield. This illustrated that the multi-stage condensation could transfer more acetic acid into the third condenser in the catalysis tests. The ketones, such as 1,2-cyclopentanedione, 3-methyl-2-cyclopenten-1-one, and 3-methyl-1,2-cyclopentanedione, increased remarkably in the presence of FCC catalysts. The dominating phenol compounds were phenol, 4-methyl-phenol, 2-methoxy-phenol, 2,4-dimethyl-phenol, 4-ethyl-phenol, 2-methoxy-4-methyl-phenol, 2-methyl-phenol, 2-methoxy-4-vinylphenol, and 2,6-dimethoxy-phenol. The use of the FCC catalyst reduced the contents of multifunctional components, such as 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 2-methoxy-4-vinylphenol, and 2,6-dimethoxy-phenol, while increased the monofunctional components, such as phenol, 4-methyl-phenol, 2,4-dimethyl-phenol, 4-ethyl-phenol, and 2-methyl-phenol. The multifunctional phenols are believed as the most likely bio-oil polymerization precursors. Therefore, the decrease of their contents favors the improvement of the stability of the bio-oil. The most abundant furan derivatives detected in the collected liquid were furfural, 2(5H)-furanone, 2,5-diethoxytetrahydro-furan, and 2,3-dihydro-benzofuran. The peak area percentages of 2(5H)-furanone and 2,5-diethoxytetrahydro-furan increased, while that of 2,3-dihydro-benzofuran decreased significantly. Moreover, it is to be pointed out that the peak area percentages of hydrocarbons increased noticeably when using FCC catalysts. This contributed to the decrease of the oxygen content of the collected liquid. There were no sugars detected in the collected liquid of the second condenser. It indicated that the multi-stage condensation units can realize the enrichment of sugars in the first condenser. In combination with Figure 7 and Table 5, it can be concluded that the optimal percentages of the catalyst in bed materials were 10% FC and 20% SC and more use of the catalyst led to little change of the compound contents of the bio-oil and a considerable decrease of the oil fraction yield because of the formation of coke on the catalyst surface.

Table 6 shows the properties of the collected liquids in the second condenser. As shown in Table 6, a more than 20%
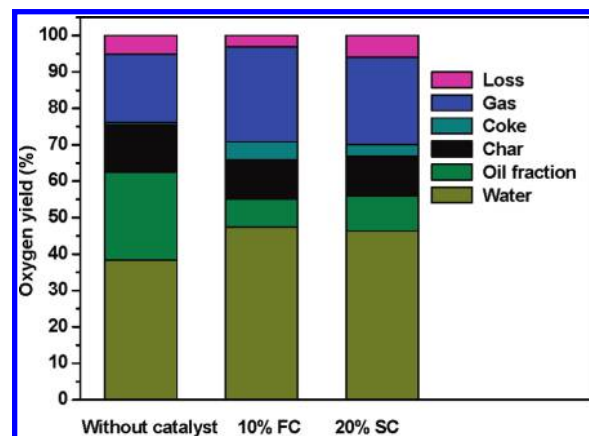
decrease in the oxygen content of collected liquid with FCC catalysts was compared to that without catalyst. The decrease of the oxygen content in oil contributed to a remarkable increase in the higher heating value (HHV) from 19.92 MJ/kg without catalyst to 34.24 and 32.67 MJ/kg with 10% FC and 20% SC, respectively. Although the oxygen content of the bio-oil with FCC catalysts is a little higher than that with HZSM-5 in our previous study,[24] its yield is higher than previously. Besides, the FCC catalysts, especially SC, have a much lower price than HZSM-5.

**Carbon and Oxygen Distributions in Pyrolysis Products.** The aim of our work is to obtain more oil fraction products with a lower oxygen content. The oxygen and carbon redistributions in pyrolysis products can show the effect of the catalysts during the catalytic fast pyrolysis process. The distribution of carbon and oxygen in pyrolysis products obtained in noncatalytic and catalytic tests are shown in Figures 8 and 9, respectively. It can be seen that both the carbon and oxygen mass balance were in the range of 85−97%. As can be observed from Figure 8, less carbon was transferred into the oil fraction in the catalytic test than that in the noncatalytic test. In the catalytic experiments, more carbon was converted into CO, $CO_2$, and coke, especially in the test using FC as the catalyst. As shown in Figure 9, a large part of oxygen was transferred into water during the fast pyrolysis process. It was obtained that 24.0% internal oxygen of feedstock was transferred into the oil fraction in noncatalytic tests compared to 7.7 and 9.7% in the catalytic experiments with 10% FC and 20% SC as the catalyst, respectively. The increase of oxygen transferred into coke in the catalytic experiments can be attributed to the increase of the coke yield. Converting oxygen into CO and $CO_2$ is an ideal route to decrease the oxygen content of bio-oil. As indicated in Figure 9, the oxygen transferred into gas increased from 18.9% in the noncatalytic experiment to 26.1 and 23.9% in catalytic experiments with 10% FC and 20% SC, respectively.

## Conclusions

In this work, biomass fast pyrolysis with different FC and SC percentages (0, 5, 10, 20, and 30%) in bed materials were conducted in a fluidized bed to determine their effects on the pyrolysis product yields and the chemical compositions of the liquid products.

The uses of FC and SC caused a remarkable decrease of the heavy oil fraction and an increase of water, coke, and noncondensable gas yields. FC showed more catalytic activation than SC at the same catalyst percentages, but the oil fraction yield was lower than that with SC because of more coke formation. Catalytic fast pyrolysis of biomass should be avoided using those catalysts with a very strong acidity to obtain a higher oil fraction yield and less coke. The optimal percentages of the catalyst in bed materials were 10% FC and 20% SC. More use of the catalyst led to little change of the compound contents of the bio-oil and a considerable decrease of the oil fraction yield.

The application of the multi-stage condensation achieved a good separation of the oil fraction and water in the liquid products. The water content of the liquids collected by the first, second, and third condensers were 5.1, 10.5, and 60.3% in the noncatalytic test while about 5−6, 10−12, and 79−82% in the presence of 10% FC or 20% SC. Most of the oil fraction obtained in the catalytic experiment was the light oil fraction collected by the second condenser.

The analysis of the collected liquid in the second condenser showed that the use of the FCC catalyst reduced the contents of multifunctional components of phenols, which are believed as the most likely bio-oil polymerization precursors. Therefore, the stability of the bio-oil should be improved. Moreover, the addition of the FCC catalyst led to a remarkable increase of the hydrocarbon content and contributed to the decrease of the oxygen content of the collected liquid.