# Hydrocarbon produced from upgrading rich phenolic compound bio-oil with low catalyst coking

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## HIGHLIGHTS

- Achieved high hydrocarbon yield (75% C) from catalytic process on liquid–liquid extracted bio-oil.
- Low catalyst coking and high catalysis efficiency was achieved, with high recovery.
- Aldehyde, ketone and other small active molecular contributed to catalyst coking.

## ARTICLE INFO

## ABSTRACT

Catalytic upgrading of raw bio-oil and liquid–liquid extracted bio-oil (high concentrated phenolic with trace acid and acetaldehyde) with methanol over ZSM-5 catalyst had been studied in this work. Temperature played vital function and leaded to increasing gas yield but less catalyst coking. It also changed both chemical distribution and selectivity on both gas and liquid products, with aromatic concentration increasing by 34.42%. Temperature of 400 °C was selected as the optimized reaction conditions with liquid yield of 10.47 wt.% and 75.00% aromatic hydrocarbon in liquid product from 100 g biomass, only with coke yield of 1.42 wt.%. Phenolic-rich extracted bio-oil obtained higher aromatic hydrocarbon yield (7.3 wt.% increased from 1.1 wt.%) and lower coke yield (1.42 wt.% decrease from 15.79 wt.%) than raw bio-oil. Catalyst regenerated from this type of feedstock also achieved higher activity and longer useable running times on aromatic yield compared to fresh catalyst. This result suggested that lignin derived phenolic and guaiacol compounds were not the only reason caused catalyst coking on ZSM-5 catalyst. Small high active molecules of acetic acid and acetaldehyde also acted as important precursors of catalyst coke formation.

## 1. Introduction

Biomass has already been regarded as an attractive feedstock to replace petroleum, to produce renewable liquid fuels called bio-oil [1–3]. Pyrolysis is a thermochemical conversion process without oxygen, which can produce liquid bio-oil at 350–650 °C [4]. Due to its complex compounds, 35–40% oxygen content and high water content, it is essential to upgrade the bio-oil before direct use [5–7]. A considerable amount of research has been conducted on bio-oil upgrading with zeolite catalyst [8–11]. Although the results of these studies are sometimes contradictory, ZSM-5 is still recognized as the most promising zeolite catalyst [12]. According to prior research, the most difficult challenge in bio-oil upgrading is catalyst coking [13]. Catalyst coking occurs at all temperatures and presents a notable increase when increasing the temperature, especially above 400 °C. Gayubo et al. [14] found formation of coke is an irreversible process [12]. The precursors of coking undergo polymerization and polycondensation on the catalytic surface and fill up the inner pores of zeolite catalyst, further contributing to inactivation of catalysts [10]. Several small molecules also repolymerize to form coke [28,29]. Among all of the chemicals in bio-oils, oxygen-containing function groups, predominantly sugars, guaiacols, and furanic rings, are most likely to form coke because of their instability and deficiency in molar balance [13,15,16]. Obviously, acid sites in the pores play an important role in the coke deposition on the catalysts. Huang et al. [24] investigated that the acid sites acted as essential part of catalyst and

donated protons to form hydrocarbon cation. The deprotonated basic framework of the zeolite offered potentials on cracking and aromatization, which promoted the catalytic deoxygenation, but resulted in coking.

Wang et al. [12] proposed that lignin derived phenolic compounds was easier to prone to coke and char than other two compounds in lignocellulosic biomass because of its complex structure and leaded to lower efficiency of carbon conversion. Nevertheless, Yu et al. [17] pointed out that a majority of lignin-derived compounds (such as coniferyl and syringyl) were too large for the pores of zeolites, as Zhang et al. [18] observed that the ZSM-5 had 0.53 × 0.56 nm for straight channel and 0.51 × 0.55 nm for sinusoidal channels. On the opposite, Carlson et al. [19] mentioned catalyst coke only could be formed on its external surface, because coke was unable to be accommodated within the narrow inner channels. Meanwhile, in our pre-studies on catalytic cracking and upgrading using pure phenol and guaiacol (2-methoxy phenol, 2-methoxy-4-methylphenol) as model compounds, much less catalytic coke yield was found, than using pyrolysis oil. It is fully possible that significant interaction occurred between the other thermal-derived products such as acid, aldehyde, ester and phenolic compounds [20–23].

Many groups are currently focusing on seeking optimized catalysis conditions to reduce coke formation during the process [3,9,11,12,25,26]. Burning the coke at high temperature during the process is possible under certain conditions to reduce coking [25]. Co-feeding non-condensable gases into the reactor is also considered to have a great potential to minimize catalytic coking, by effectively reducing partial pressure, which leads to enhanced acidity and cracking activity of the catalyst to avoid catalytic coking [11,26]. Nevertheless, literature results indicated that burning, co-feeding with hydrogen and water, controlling reaction temperature, or reducing the acidity of the catalyst cannot drive down coking on the catalyst remarkably [25]. It is still a significant challenge to minimize coking at mild reaction conditions.

The phenolic compounds in bio-oil come not only from lignin, but also cellulose and hemicellulose. Bu et al. [2] obtained a higher phenol yield from lignocellulosic biomass than model compound lignin under similar reaction conditions and furan ring compounds derived from cellulose and hemicellulose could also be converted into aromatic during catalytic pyrolysis on ZSM-5 catalyst. Our prior research has shown that liquid–liquid extraction using chloroform solvent on the water phase has had a significant effect in eliminating acid, alcohol and sugar compounds from the chloroform solvent phase [27]. In this work, we determined how ZSM-5 catalyst worked with a higher phenolic concentrated bio-oil extracted solution in a micro scale reactor. The self-design micro scale reactor pumped atomizing feedstock directly into high temperature systems, to avoid bio-oil coking during the feedstock heating period. Comparison had been placed between the catalyst coking condition and hydrocarbon product yield between different feedstock of raw bio-oil mixed with 50 wt.% methanol (RB) and phenolic-rich bio-oil fraction with 50 wt.% methanol (PB). The objective was to give an overview of the reaction conditions for maximum hydrocarbon yield with low coking from bio-oil on ZSM-5 catalyst, and found the correlations between small active molecular such as aldehyde and catalyst coking.

## 2. Experimental

### 2.1. Catalyst and feedstock preparation

Methanol (Extra dry, SC, 99.8%) was purchased from Fisher Scientific. Zeolite (CBV 5524G) was purchased from Zeolyst International. The ZSM-5 zeolite was activated with water, and

then dried in an oven at 105 °C for 12 h. After water was removed from the mixture, the catalyst was calcined at 550 °C for 5 h before use. Catalyst regeneration was conducted by calcining in a furnace at 550 °C for 3 h and sealed storage before testing.

The RB was produced via microwave pyrolysis of Douglas fir pellet (cellulose 41%, hemicellulose 21%, lignin 32%) at 450 °C, for 25 min and a fixed microwave power input of 700 W on a Sineo MAS-II batch microwave oven (Shanghai, China) with a rated power of 1000 W. The rest solid after pyrolysis are weighted as the mass of solid product. RB was the liquid collected by cooling condenser and the rest was gas product. PB was obtained by a liquid–liquid extraction using RB as feedstock, and weighted after solvent distillation [27]. The bio-oil obtained from microwave pyrolysis was collected, following treated by the liquid–liquid extraction process (chloroform solvent), and the oil phase was stored in a sealed bottle in a freezer. Both RB and PB were mixed with 50 wt.% ratio of methanol for dilution before use. The product yields and main components of these two types of feedstock are list in Table 1.

### 2.2. Experimental method

The catalytic upgrading process was conducted in a self-designed continuous fixed bed reactor, showed in Scheme 1. The reactor contained a vessel, a 10 mL container, a metal tube (inner diameter of 0.64 cm) heated by a split heater, condensers and three valves. Before the experiment, the ZSM-5 catalyst was loaded in the metal tube in a ratio of 5 wt.% to bio-oil feedstock (100 g PB or RB). The catalyst was heated to the set temperature (from 350 to 450 °C) with a heating rate of 1 °C/s in a nitrogen atmosphere. Each time, 10 mL of bio-oil was pumped into the hot catalyst tube controlled by the container and valves A, B. After 1 min retention time, valve C was opened and the mixture was separated via the condensers. The operation repeated ten times until all the 100 g of bio-oil feedstock took reaction with the catalyst. The non-condensable gas was immediately characterized after collection. After finish the experiment, the carrier gas was pumped into the tube to blow out the upgraded bio-oil. At the end of the experiment, the metal tube was removed from the system and the catalyst was collected for further characterization, regeneration and reuse.

**Table 1**
Product yield and chemical distribution of RB and PB.

| Product distribution | Bio-oil (RB) | Gas | Solid |
|---|---|---|---|
| Yield (Biomass 100 g) (g) | 38 | 32 | 30 |
| After solvent extraction | Bio-oil (RB) | Extracted-oil (PB) | Water-phase |
| Yield (Biomass 100 g) (g) | 38 | 13 | 25 |
| Water content (wt.%) | 64.51 | 9.20 | 93.26 |

| Chemicals (base on chemical mole) | RB (%) | PB (%) |
|---|---|---|
| Acids: | 3.48 | 0 |
|    Acetic acid | 3.01 | – |
| Aldehyde/ketone | 9.41 | 3.34 |
|    Acetaldehyde | 7.96 | 0 |
|    1,2-Cyclopentanedione, 3-methyl- | 1.07 | 1.86 |
| Alcohols | 1.41 | 0.09 |
| Phenol | 4.52 | 4.07 |
| Guaiacols | 54.50 | 72.02 |
|    Phenol, 2-methoxy- | 8.86 | 10.36 |
|    Phenol, 2-methoxy-4-methyl- | 17.20 | 29.09 |
|    Phenol, 4-ethyl-2-methoxy- | 7.94 | 20.54 |
| Furan ring compounds | 17.59 | 20.46 |
|    Furfural | 10.08 | 17.49 |
|    2-Furancarboxaldehyde,5-methyl- | 2.86 | 0 |
|    Furan,tetrahydro-2,5-dimethoxy- | 0.53 | 0.13 |
|    2-Furanmethanol | 3.36 | 0 |
| Esters | 2.72 | 0 |
| Sugars | 0.73 | 0 |
| Total | 100.00 | 100.00 |