



## Catalytic cracking of biomass pyrolysis tar over char-supported catalysts

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### ABSTRACT

The work aims to investigate an effective method of catalytic reforming of tar during biomass high-temperature pyrolysis using rice husk char (RHC) and metal impregnated (Fe, Cu and K) char in a dual-stage reactor. The char and char-supported catalysts exhibited high catalytic performance, in terms of the high tar conversion efficiencies of 77.1% for RHC, 82.7% for K-RHC, 92.6% for Fe-RHC and 90.6% for Cu-RHC at 800 °C. Moreover, K-RHC and Cu-RHC catalysts after three cycles still exhibited high activity for tar removal. The catalytic tar conversion by char or char-supported catalysts contributes to improving the yield of syngas, particularly the combustible gases of H<sub>2</sub>, CO and CH<sub>4</sub>, corresponding to the syngas yield increasing from 196.6 mL/g for thermal reforming to 269.6 mL/g for K-RHC, 274.9 mL/g for Cu-RHC and 342.7 mL/g for Fe-RHC at 800 °C, respectively. The results from GC-MS analysis illustrated that the addition of char and char-supported catalysts promoted the transformation of larger polycyclic aromatic hydrocarbons into lighter tar compounds, leading to an increase in the proportion of single-ring tars. XRD results indicated that the most active phases of the fresh K-RHC, Cu-RHC and Fe-RHC for tar cracking and reforming were KCl, Cu and Fe, respectively. Textural characterization showed the addition of Fe and Cu was in favor of producing highly porous carbon materials and led to the increase in specific surface area and total pore volume.

### 1. Introduction

Rice husk (RH) as a typical agricultural residue is abundant in China, and it has been treated using traditional methods such as composting and incineration [1,2]. However, these methods are not suitable to deal with this biomass waste as rice husk contains small concentrations of nitrogen for composting and a considerable amount of solid grains that would generate smoke into the environment during incineration [3]. The administration of environment must keep up with the improvement of more efficient and environmentally-friendly techniques. The double pressures of economy and ecology make it imperative to utilize various thermochemical techniques, such as pyrolysis and gasification, to convert biomass into high value products. Pyrolysis or gasification is a practical method to generate combustible syngas using rice husk. The syngas can be not only burned for electricity generation but also further turned into liquid transportation fuels. However, during biomass pyrolysis and gasification, some unwanted by-products such as NO<sub>x</sub>, fly ash and tar are unavoidable. Particularly, the formation of tar represents one of the critical problems for the commercialization of biomass pyrolysis or gasification technology.

Biomass tar, a complex mixture of various organic compounds, can condense on the surface of filters, engines and heat exchangers and thus brings lots of negative effects to the stability and security of the whole

system [5]. Moreover, aromatic compounds in tars such as polycyclic aromatic hydrocarbons (PAHs) and benzene are toxic and the ecosystem will be harmed if it is discharged into the environment. As a consequence, the efficient removal of tar is essential for gaining clean syngas from biomass and increasing the process efficiency. Several methods have already been examined for removing tar from the syngas, including physical method [4], thermochemical treatment (e.g., thermal cracking [5], catalytic reforming [6,7] and plasma-assisted cracking [8]). Physical treatment of tar by absorption (e.g., water and oil) is the least complicated way to remove tars, while is not acceptable as a result of losing the chemical energy contained in tars and causing secondary pollution if the wastewater contaminated by tar is discharged into the environment [9]. Conversion of tar by thermal cracking/reforming is generally preferred, since the tar is decomposed into permanent fuel gases and its energetic value remains in the gas phase. Thermal cracking of tar is generally conducted at relative high temperatures (> 800 °C), and therefore large energy input, thermally resistant reactor materials and long residence times are required [10]. Catalytic reforming process which can realize tars degradation at temperatures of 600–900 °C is considered as the most promising in practical applications of biomass due to reliability and fast reaction rate [11].

To date, a great number of catalysts, including natural minerals

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(dolomite [12], shells [13] and olivine [14]), alkali species [15,16], nickel-based catalysts [6,17] and non-nickel transition metal catalysts [18,19], have been extensively developed and studied for removal of pyrolysis tar. In general, dolomite, olivine, zeolites and  $\text{Al}_2\text{O}_3$  are frequently used as catalysts support, among which olivine and dolomite are found to be attractive because of their lower costs and relative abundance in different regions [20]. However, these catalyst supports have inferior catalytic activity for tar conversion and are prone to deactivation caused by coke formation, and preparation processes of catalysts are time and energy consuming, leaving room for betterment [21]. Recently, char or char-supported catalysts derived from biomass or coal pyrolysis were found having good catalytic activity for tar decomposition. Char itself shows fair tar catalytic activity due to inorganic elements on the surface, such as K, Fe, etc. Wang et al. [22] reported that hot char-catalytic reforming of the volatiles leads to an increase in the dry syngas yield, while the yield of pyrolysis liquid products decreased and molecular weight of the oil became lighter. In our previous study [23], char and char-supported potassium catalysts were found having good activity for tar elimination due to the good absorbability of char and catalytic property of potassium. Min et al. [24] presented that char would not only disperse the catalysts but also interact with the catalysts to enhance their activity for the steam reforming of tar. The deactivated char or char-supported catalysts can be simply gasified during the tar reforming process to recover the energy without the need of frequent regeneration, while the char itself has unfixed properties depending upon biomass type and preparation conditions [25].

Char-supported nickel catalysts have been commonly used in biomass gasification due to their high tar reforming activity, which lead to high yields of synthesis gas [26,27]. One limitation of Ni-based catalysts is their rapid deactivation by carbon deposits or sulfur poisoning. Furthermore, nickel compounds are generally toxic which may caused environmental problems [28]. K-based, Cu-based and Fe-based catalysts have also been attracted more attention, since they are much cheaper and environmental friendly [29,30]. Kaewpanha et al. [29] studied calcined waste scallop shell supported copper catalysts for steam reforming of biomass tar. It was found that Cu supported on scallop shell catalysts exhibited high catalytic activity on tar reforming. Wang et al. [31] observed that the Fe-loaded char showed good catalytic performance on bio-oil reforming, while the catalytic performance depended on the preparing conditions. It has also been reported that the presence of alkali and alkaline earth metals (AAEMs), iron or copper was beneficial to tar in-situ or ex-situ conversion [32,33]. In view of the above mentioned studies, it is expected that the low-cost biomass char-supported catalysts, using a variety of metals, would be capable to decompose tar to a significant conversion level at relative low temperatures ( $\leq 800$  °C). Meantime, further investigations focusing on char and metals evolution are vital to understand the catalytic mechanism of the char supported catalysts.

The objective of this work is to synthesize K, Fe and Cu catalysts on the basis of biomass in-situ char and then examine the process of char formation and metallic elements evolution during catalysts preparation. The catalytic effects of the synthesized char-supported catalysts (K-RHC, Cu-RHC and Fe-RHC) on the cracking and reforming of primary volatile product from rice husk pyrolysis were investigated using a dual-stage fixed bed reactor. The variation of tar composition and catalysts structural characteristics was examined to further understand the catalytic mechanism of char.

## 2. Experimental methods

### 2.1. Biomass material

Rice husk (RH), collected in Xuzhou, Jiangsu province, was chosen as the biomass feed stock in this study. The rice husk was crushed and then sieved to obtain a particle size of 0.18–0.43 mm prior to being

**Table 1**  
Ultimate and proximate analyses of RH and RHC.

Sample	Ultimate analysis (wt.%, daf)					Proximate analysis (wt.%, db)		
	C	H	O <sup>a</sup>	N	S	Volatile	Fixed carbon	Ash
RH	35.6	7.2	56.7	0.4	0.1	56.4	18.4	25.2
RHC	50.6	0.6	48.7	0.1	0	14.3	37.7	48.0

Db – Dry basis; daf – Dry and ash free basis.

<sup>a</sup> By difference.

dried at 105 °C for 24 h. Table 1 gives information about the ultimate and proximate analyses of the RH analyzed by an elemental analyzer (Vario Micro Cube, Elementar, Germany), and the rice husk char (RHC) obtained from pyrolysis at 700 °C for 30 min was also examined for comparison. The X-ray fluorescence analysis (XRF, Axios mAX, Holland) was used for examination of the chemical compositions of the ash, as shown in Table 2.

### 2.2. Catalysts preparation

Char-supported metal catalysts were prepared by the combination of impregnation and facile one-step pyrolysis. The addition of metal chlorides generally increases the char yield during biomass pyrolysis and some metal chlorides may have a synergetic effect between biomass inherent minerals and the chemicals added, which is in favor of char-supported catalysts preparation [2,34]. Meanwhile, some metal chlorides have positive effect on the increase of microporous char surface area, which is also conducive to disperse the active components [35]. Thus, KCl,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was used to prepare char-supported metal catalysts. 50 g dried RH was first immersed in 500 mL of KCl,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  solution with concentration of 0.5 mol/L, followed by being stirred for 48 h. The resulting mixtures were filtered and dried at 105 °C for about 24 h. The impregnated RH samples were pyrolyzed under a constant  $\text{N}_2$  (99.9%) flow rate of 300 mL/min from ambient temperature to 800 °C at a heating rate of 20 °C/min in a fixed bed and then kept stable for 60 min. The fixed bed reactor is made of quartz glass, with 30 mm in inner diameter and 560 mm in total length. The reactor consists of a porous sintering quartz plate at 310 mm from the top. Subsequently, the char-supported metal catalysts were obtained and defined as K-RHC, Cu-RHC and Fe-RHC, respectively.

### 2.3. Experimental apparatus and procedure

The experimental setup used for a lab-scale catalytic tar reforming is depicted in Fig. 1. Experiments were carried out under atmospheric pressure in a two-stage quartz fixed-bed reactor, which was heated externally by a two-zone electrical furnace (3 kW, 220 V). The reactor is 30 mm in inner diameter and 875 mm in total length and two sintered porous quartz plates are used to support biomass samples and catalysts. The upper quartz plate is at 350 mm from the top of the reactor and the lower is at 575 mm from the top. Both its upper and lower stages have an effective heating height of 200 mm.

Three grams of catalyst was pre-loaded into the lower stage and five grams feedstock was pre-loaded into the sample feeder prior to each experiment. The upper stage of the reactor was initially heated up to 600 °C for biomass pyrolysis and then the temperature of reforming zone was controlled from 600 to 800 °C at intervals of 100 °C. Nitrogen was used as carrier gas and passed continuously through the reactor with a flow rate of 300 mL/min to prevent any oxidation during the heating progress. After the reforming zone reached the target temperature in each test, the sample in the feeder was put into the pyrolysis zone rapidly (within 4 s). The volatile matters, such as tar and syngas, released in the form of vapor and were carried to the reforming zone by

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