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## *In-situ* catalytic conversion of tar using rice husk char-supported nickel-iron catalysts for biomass pyrolysis/gasification



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### ABSTRACT

This paper aims to propose an effective tar conversion approach during biomass pyrolysis via *in-situ* dry reforming over rice husk (RH) char and char-supported Ni-Fe catalysts. Utilizing high pyrolysis temperature, tar from biomass pyrolysis could be removed effectively in the gasifier by mixing with the char-supported catalysts, simplifying the follow-up tar removal process. Under the optimized conditions, the conversion efficiencies of condensable tar can reach about 92.3% and 93% using Ni-Fe char (without calcination) and Ni char (with calcination), respectively. It is noteworthy that the condensable tar could be catalytically transformed into the non-condensable tar or small molecule gases resulting in the heating value increase of gaseous products to benefit of the power generation systems. Compared with the other catalysts preparation methods, Ni-Fe char exhibited more advantages of convenient and energy-saving. In the presence of catalysts, the concentration of CO<sub>2</sub> (vol.%) was reduced slightly, while the CO concentration (vol.%) increased greatly because of dry reforming. Due to carbon loss, parts of RH char-supported catalysts (C-SiO<sub>2</sub> catalysts) could be converted into SiO<sub>2</sub>-based catalysts because of high-content amorphous nano-sized SiO<sub>2</sub> in RH char. In addition, partial metal oxides or ions via carbon (i.e., biochar) and gas (i.e., H<sub>2</sub>, CO) *in-situ* reduction were transformed into metallic states contributing to the enhancement of tar conversion. Therefore, RH char plays two significant roles during the process of biomass pyrolysis. On one hand, it works as an intermediate reductant to reduce the metal oxides and CO<sub>2</sub>; on the other hand, it can be considered as an adsorptive-support to adsorb metal ions and tar. After that, the char-supported catalysts could be used for tar conversion. In particular, since the metal catalysts still remain in the solid residues, the pyrolysis char could be regenerated via thermal regeneration using waste heat or gasified into syngas directly.

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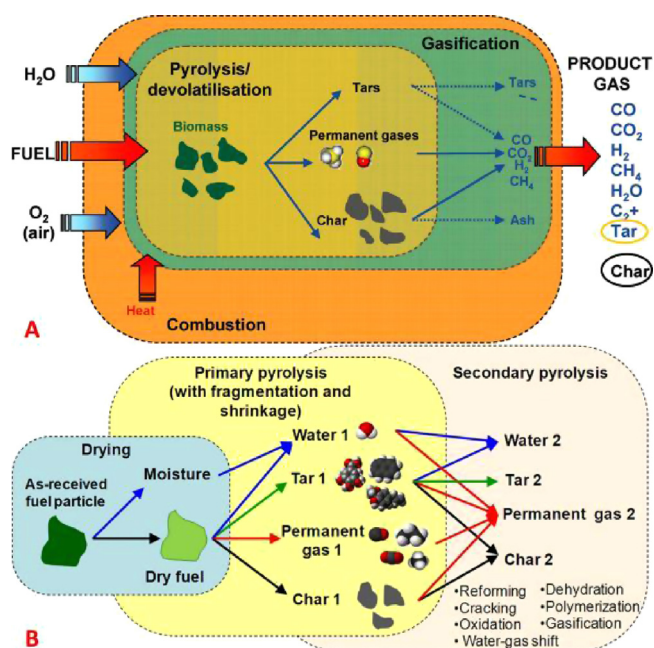
### 1. Introduction

Biomass pyrolysis/gasification is considered as one of the most promising technologies for production of sustainable fuels that can be used for power generation systems or syngas applications. Gasification of biomass has several environmental advantages over fossil fuels, namely lower emission of CO<sub>2</sub> and other flue gases such as H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>x</sub> [1–4]. Biomass gasification is a process in which biomass undergoes incomplete combustion to produce a gas product called syngas that consists mainly of H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>

(if air is used in combustion) in various proportions. Biomass gasification has many advantages over direct combustion. It converts low-value feedstocks to high quality combustible gases, which can be not only directly burned or used for electricity generation but also turned into liquid transportation fuels [5].

Processes occurring during biomass gasification are illustrated in Fig. 1A, the main processes are distinguished: drying and devolatilization, volatile and char combustion, and gasification and tar reforming with steam and CO<sub>2</sub>. These processes can be identified in certain spatial regions in fixed bed gasifiers [6]. As shown in Fig. 1B, during transient heating of the particle, temperature increases locally, leading first to the evaporation of moisture (drying stage) and then to the progressive release of pyrolytic volatiles (primary pyrolysis stage). The primary volatiles are produced from

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**Fig. 1.** (A) Main processes during biomass conversion in a gasifier: drying and devolatilization, volatile and char combustion, and gasification and tar reforming with steam and CO<sub>2</sub> [10]. (B) Thermal degradation of a solid biomass particle under inert atmosphere: drying, primary pyrolysis and secondary pyrolysis [9].

the thermal scission of chemical bonds in the individual constituents of biomass, which are cellulose, hemicellulose, lignin and extractives, and comprise permanent gas species (e.g., CO, CO<sub>2</sub>, CH<sub>4</sub>) and condensable species at ambient conditions (several organic compounds and water). Although each of the biomass constituents decompose at faster rates in different temperature ranges, the overall primary pyrolysis stage is complete at relatively low temperatures (<500 °C), yielding a carbon-rich non-volatile solid that is called char or charcoal. The produced char also contain a significant part of the mineral matter originally present in the parent fuel. Nevertheless, if the fuel is converted at higher temperatures some of the primary volatiles released inside the particle can further participate in a variety of secondary reactions to form product “2”. Serial and parallel reactions can take place, occurring either heterogeneously or homogeneously, such as cracking, reforming, dehydration, and so on [7–9].

organics (i.e., polycyclic aromatic hydrocarbons) referred to as “tar” are produced along with syngas during biomass gasification and their contents vary from 0.5 to 100 g/m<sup>3</sup> depending on the type and design of gasifier, feedstock types, and operating conditions [10]. Tar is a generic term comprising all organic compounds present in syngas except for gaseous hydrocarbons. Tars can condense to more complex structures in pipes, filters, or heat exchangers of downstream equipment and processes, which may cause mechanical breakdown of the entire system. Tars may also deactivate catalysts in the refining process. Tar removal by efficient adsorption and reforming to syngas should be important and indispensable to commercialize this technology for applications in power generation and synthetic fuel production [11]. It is essential to reduce the level of tars to enable widespread utilization of syngas. Several approaches for tar elimination, such as physical treatment [12–14], thermal cracking [15], plasma-assisted cracking [16], and catalytic reforming [17–21], have been widely reported. Among these, catalytic reforming is considered the most promising in large-scale applications because of its fast reaction rate and reliability [21] and its ability to increase the quantity of usable gases such as CO and H<sub>2</sub> in syngas.

Various types of catalysts such as calcined rocks [22], zeolites [23], iron ores [24], alkali metals [25], Ni-based catalysts [26,27], and noble metals [28–32] have been studied for their usefulness on tar removal in biomass gasification. For catalytic reactivity and economic reasons, Ni-based catalysts are considered the most promising for tar removal and syngas reforming [33–39]. Nickel catalysts are usually supported by metal oxides (e.g., Al<sub>2</sub>O<sub>3</sub> and MgO) or natural materials (e.g., dolomite, olivine, activated charcoal) [40–45]. These supports are relatively expensive, and the catalyst preparation steps are time and energy consuming; these factors limit extensive application of Ni-based catalysts. As a promising alternative, chars have been reported to be an inexpensive catalyst with fair performance in tar removal [46–49] and also an excellent adsorbent [50]. The char-supported catalysts would have low costs and be simply gasified to recover the energy of the char without the need of expensive regeneration after deactivation. However, the disadvantages of biomass char are consumption because of gasification reactions and unfixed properties depending on biomass type and process conditions.

Recently, Wang et al. [51] investigated char and char-supported nickel catalysts for secondary syngas cleanup and conditioning. In this study, Ni-based catalysts were made by mechanically mixing NiO and char particles at various ratios. The Ni/coal-char and Ni/wood-char catalysts removed more than 97% of tars in syngas at 800 °C reforming temperature, 15% NiO loading, and 0.3 s gas residence time. Meanwhile, iron-based catalyst and additive Fe have attracted more attention of researchers. Nemanova et al. [52] reported the use of Fe based catalysts and the effect of iron-based granules on biomass tar decomposition. The use of these Fe based catalysts resulted in tar reduction. Liu et al. [53] studied the effect of different additives (Fe, Mg, Mn, Ce) on catalytic cracking of biomass tar over Ni<sub>6</sub>/palygorskite. The result also demonstrated Fe played a better role in improving the reactivity of Ni<sub>6</sub>/palygorskite.

Fe-based catalysts [54] are much cheaper, abundant and environmental friendly than Ni-based or other metal catalysts. Moreover, iron oxides possess various physicochemical properties, e.g., Fe<sub>2</sub>O<sub>3</sub> (oxidation), Fe<sub>3</sub>O<sub>4</sub> (magnetism), possibly enhancing the catalytic activity or decreasing the coking deposition. In the previous work, bimetallic catalysts, such as Fe–Co, Ni–Co alloy particles supported in Al<sub>2</sub>O<sub>3</sub>, were benefit for steam reforming of tars compared with Fe/Al<sub>2</sub>O<sub>3</sub> and Co/Al<sub>2</sub>O<sub>3</sub> [55,56]. However, the rice husk (RH) char-supported bimetallic Ni–Fe catalysts have been rarely reported for tar conversion. In this work, we proposed a novel biomass catalytic pyrolysis technology for *in-situ* tar conversion and upgrading using RH char and char-supported Ni or Fe catalysts.

## 2. Materials and methods

### 2.1. Biomass and char characterization

The biomass feedstock of RH was collected from Thailand. The ultimate and proximate analyses of RH and RH char shown in Table 1 were conducted by elemental analyzer (Vario MICRO Cube, Elementar, Germany) and DTG-50 (SHIMADZU, Nakagyo-ku, Kyoto, Japan), respectively. Besides, the chemical composition of rice husk ash (RHA) was analyzed by X-ray fluorescence “XRF” (SHIMADZU, Rayny EDX 700, Japan).

### 2.2. Catalysts preparation

RH char was prepared by slow pyrolysis at the temperature of 700 °C in the N<sub>2</sub> atmosphere. Three types of Ni char (Ni<sup>2+</sup>: 0.2 mol/L), Fe char (Fe<sup>3+</sup>: 0.2 mol/L) and Ni–Fe/char (Ni<sup>2+</sup>: 0.1 mol/L,

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