



Steam gasification of safflower seed cake and catalytic tar decomposition over ceria modified iron oxide catalysts



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ABSTRACT

Catalytic steam gasification of safflower seed cake was carried out using a double-bed microreactor in a two-stage process in the presence of ceria oxide (CeO₂) modified iron oxide (Fe₂O₃) catalysts with different CeO₂–Fe₂O₃ ratios. The effects of both catalyst and the temperature of catalytic bed on the tar decomposition and the overall gaseous product yield were investigated comparatively. It was found that ceria modified iron oxide catalysts had higher reactivity than that of the individual Fe₂O₃ and CeO₂ for the catalytic tar decomposition in safflower seed cake steam gasification. The CeO₂–Fe₂O₃ catalyst with 50 wt.% of Fe₂O₃ exhibited the excellent performance for tar conversion at 700 °C. A comparison of tar decomposition from thermal run and catalytic run showed that in thermal run tar decomposition was progressed via steam reforming only. However, in the presence of catalyst, tar decomposition occurred via both steam reforming and water gas shift reaction. As a conclusion, ceria promoted iron catalysts were found to be active for both hydrogen production and tar decomposition in steam gasification of lignocellulosic biomass.

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1. Introduction

Conversion of lignocellulosic biomass to synthesis gas is one of the important technologies for the energy utilization of biomass as renewable organic resources. Biomass gasification is one of the most promising thermochemical processes to produce syngas and fuel gas. There are many studies of biomass gasification using different agents such as carbon dioxide (CO₂), steam, and air. Steam gasification has more advantages among the other agents. Some studies showed that the steam gasification reaction is much faster than the CO₂ gasification [1]. Furthermore, for steam gasification, the produced gas contains hydrogen (H₂) and carbon monoxide (CO) which can be used as fuel gas or raw material for chemical synthesis depending on the gas composition [2]. The use of steam increases hydrogen production due to the water–gas–shift, steam reforming and water–gas reactions.

The main problem of gasification in general is the formation of tar, since it creates severe problems in syngas utilization. Tar formed during gasification is removed by physical methods, using various types of filter or scrubber and cyclones [3]. On the other hand, catalytic decomposition can be considered as the best promising technique for tar elimination because they can be also converted into useful products besides completely destroyed. In literature, considerable research concerning the catalytic decomposition of tar has been undertaken and several

types of catalysts have been tested to decompose tar either in bed as primary catalysts [4,5] or in downstream reactor as secondary catalyst [6–8].

Nickel-based steam reforming catalysts, well known and commercially available, have been proven to be very active in tar reduction. But the catalyst deactivation due to the sintering and/or coke deposition is one of the serious problems for nickel (Ni) catalysts. Besides Ni catalysts, dolomites and olivine have been extensively investigated as biomass gasification catalysts [9,10] because they are inexpensive and abundant and can reduce the tar content of the product gas. They can be used as a primary catalyst (in bed) as well as secondary, downstream. But they have some drawbacks. For example, they are significantly active above 800 °C which is not a desirable temperature if catalyst is used as secondary catalyst. In addition, their activity depends on iron(III) oxide (Fe₂O₃) contents. It was found that a different dolomite has different activities due to the different Fe₂O₃ contents and pore diameters [11,12].

The iron based catalysts are another important group of active catalysts and have been applied extensively for biomass gasification and tar conversion [13,14] because of their high tar destruction activity, as well as the reforming of light hydrocarbon activity. Uddin et al. have developed [13] iron-based catalysts for the decomposition of tar derived from cedar wood gasification in a two stage reactor by steam reforming. The tar was decomposed to hydrogen rich gasses over the iron oxide catalysts by water gas shift reaction. It was suggested that the reduced iron species are the active sites on iron oxide catalysts in steam

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reforming [15]. Matsuoka et al. also reported that the addition of iron promoted hydrogen formation in the decomposition of tar derived from steam gasification of wood chips over iron/alumina catalysts [14, 16].

Although, for the Ni, catalyst deactivation due to coke deposition could be a serious problem, it was found that the addition of ceria (Ce) into the nickel (Ni) catalysts promoted the gasification of the deposited carbon, which led to increase in the stability of the catalyst, as well as the water–gas shift reaction, and as a result, the stability of the catalyst was improved [17]. Ceria oxide (CeO_2) can be considered as a promoter, which increases activity and/or selectivity, and a support that provides the dispersion of the active phase [18]. It was reported that lattice oxygen from the ceria support could oxidize carbon produced from methane decomposition resulting in the formation of CO and maintaining the catalytic activity of Ni– CeO_2 [19]. Zhang et al. investigated the effect of ceria addition to a Ni/olivine catalyst for steam reforming of benzene or toluene and they found that CeO_2 addition to Ni/olivine enhanced tar conversion, H_2 production, and coke resistance [20]. In the case of steam reforming of bio-oil, it was found that ceria–zirconia supported catalysts are more active than those alumina-supported, both in terms of carbon oxides (CO_x) yield and hydrogen production [12]. Asadullah et al. performed catalytic gasification of cellulose [21] with the Rh/ CeO_2 /M (M: SiO_2 , Al_2O_3 , and ZrO_2) type catalysts with various compositions, the conventional nickel and dolomite catalysts in a fluidized bed gasifier at 500–700 °C. They reported that CeO_2 is very effective to the enhancement of carbon conversion and Rh catalyst provided much better results than conventional Ni and dolomite catalysts. Ceria has well-known redox properties, shows promising catalytic activities and selectivity in partial oxidation because of its oxygen storage ability on the basis of $2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + 1/2\text{O}_2$. It was suggested that reduced Ce species can be oxidized with steam, and CeO_2 can be regenerated [22]. It has also the ability to promote metal–ceria interaction and metal dispersion [23]. The redox features of ceria could be greatly enhanced by the addition of transition metals as well as noble metals, and the improvement in catalytic performance was often attributed to the strong metal–ceria interaction and the generation of metal–ceria solid solutions. CeO_2 has also been reported to prohibit coke deposition on catalysts [6,24,25]. In literature, ceria supported catalyst has been used mainly in the gasification of bio-oil derived from biomass pyrolysis and bio-oil model compounds. Therefore, the use of CeO_2 as support and catalyst promoter is an interesting application for steam gasification of biomass.

On the basis of the above literature reports, combined application of CeO_2 and Fe_2O_3 catalysts looks promising. The present work follows from the previous investigation on catalytic decomposition of biomass tars with iron oxide catalysts carried out by Uddin et al. [13]. In the present study, ceria modified iron catalysts with varying amounts of iron (from 10 to 90%) were prepared and used in steam gasification of safflower seed cake. One of the aims of this study is the tar conversion during gasification of safflower seed cake, as well as hydrogen production.

2. Material and methods

2.1. Materials

Safflower seed cake (a by-product of safflower oil production) was provided by an oil company (Sivas, Turkey). It was ground to particle size less than 2 mm and then dried overnight at 105 °C. The proximate, ultimate and component analyses of seed cake are shown in Table 1. Thermogravimetric analysis of biomass showed that volatilization occurred between 250 and 500 °C and then the weight loss reached a plateau after about 500 °C.

CeO_2 – Fe_2O_3 with different ratios was prepared by coprecipitation method using ammonia as precipitating agent. Starting materials were iron nitrate hexahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and cerium nitrate

Table 1
Some properties of safflower seed cake.

Proximate analysis [as received, wt.%]	
Moisture	11.2
Volatile matter	70.3
Fixed carbon	15.6
Ash	2.9
Ultimate analysis [dry, wt.%]	
C	49.8
H	5.8
N	3.4
S	0.2
O ^a	40.8
Component analysis, [dry, wt.%]	
Cellulose	22.5
Hemicellulose	39.5
Lignin	33.5
Extractives	4.5

^a Calculated from difference.

hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). 20 wt.% of the iron salt or the mixture of the salts is added to a required amount (10% in excess of the stoichiometric amount) of 7 wt.% ammonia water solution quickly and stirred vigorously. The precipitate was washed with deionized water. The precipitate was then filtered and dried at 110 °C for 24 h and calcined at 700 °C in air for 1 h. The calcined samples were crushed and sieved into an average size of 0.367 mm. The various CeO_2 – Fe_2O_3 catalysts were referred to as x% CeO_2 –y% Fe_2O_3 , in which x and y are the weight percentage of CeO_2 and Fe_2O_3 , respectively.

The surface area and bulk density of the investigated catalysts are shown in Table 2. The powder X-ray diffraction (XRD) pattern of the catalysts was recorded using a Shimadzu XRD-6100 diffractometer with $\text{CuK}\alpha$ irradiation (30 kV, 30 mA).

2.2. Gasification setup

Gasification of biomass is carried out in a two stage (fixed-bed) quartz reactor. The schematic diagram of experimental set-up has been given in the previous study [13]. The experimental procedure involved the following steps: in a typical run, a very small amount of biomass sample (0.04 g, particle size: 0.15–0.30 mm) was placed in the top section on a quartz wool bed and the desired amount (0.065 ml) of catalyst was placed on the second quartz wool bed. The reactor system was purged with nitrogen (N_2) flow for 30 min, while a mixture of water vapor (H_2O) generated in a bubbler at 70 °C and N_2 with a composition of 30% H_2O – N_2 at flow rate of 20 cm^3 STP (Standard Temperature and Pressure)/min was passed through the reactor bypass. Both nitrogen and steam flows were chosen based on the previous study [13] in this reactor system. In the meantime, the bottom bed (catalyst bed) was heated to the predetermined temperature (600–850 °C) at rate of 3 °C/min in N_2 flow. When the bottom bed (catalyst bed) temperature reached the desired temperature, heating of the top bed (biomass bed) to the 850 °C commenced at a heating rate of 3 °C/min and a

Table 2
Surface area of catalysts.

Catalyst	Surface area (m^2/g)
100% Fe_2O_3	1.7
10% CeO_2 –90% Fe_2O_3	11.2
30% CeO_2 –70% Fe_2O_3	11.4
50% CeO_2 –50% Fe_2O_3	11.2
70% CeO_2 –30% Fe_2O_3	16.5
90% CeO_2 –10% Fe_2O_3	31.7
100% CeO_2	33.8

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