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Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



# The influence of catalysts in biomass steam gasification and catalytic potential of coal bottom ash in biomass steam gasification: A review

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### ARTICLE INFO

Keywords: Biomass steam gasification Dolomite Nickel catalyst Alkaline metals Coal bottom ash

#### ABSTRACT

Biomass gasification appears as a potential source of renewable and sustainable energy for green environment. Biomass steam gasification has gained significant importance in this era due to high product yield and economical viability. For commercialization of biomass steam gasification process, suitable catalyst for tar reduction, higher product yield and active life of catalyst are still hot questions. Different types of catalyst like dolomite, alkaline metal, nickel and olivine are used in biomass steam gasification. Some of them have good potential for tar elimination and others are good in higher product yield. Most of the catalysts have short active life, expensive and with regeneration problem. The purpose of current study is to review the effect of different catalysts in the biomass steam gasification process used for tar elimination and higher product yield. In addition, the potential of coal bottom ash as a substitute of catalyst in biomass steam gasification is discussed.

#### 1. Introduction

The fast growth in world population and rapid urbanization along with increasing developments in world economies has escalated the energy demand in the last century [1]. The utilization of fossil fuels to meet that energy demand plays a capital role in greenhouse gas emissions [2]. It is also the significant cause of global warming that rattled the weather cycle of major part of the world. The three major concerns including energy, economy and environment have triggered research for alternative, renewable and sustainable sources of energy around the world [3]. Biomass comes forward as a prior source of energy among other resources like solar and wind energy. Moreover, among the renewable resources, it is the only one which can be converted into liquid and gaseous fuel and used as raw material for the production of chemicals like methanol, ethanol and higher hydrocarbon [4,5]. The utilization of biomass-based fuels have not only the advantage of reducing carbon footprints but also reduce the dependence on fossil-based fuels, have a good impact on the agriculture sector and minimize the solid municipal waste as well [7]. The world production of biomass is 1880 billion tonne/year and it has 14% share of world energy production [8].

Biomass can be converted into products by biological and thermochemical conversion. Thermochemical conversion is a better route than biochemical due to higher amount of feedstock and faster conversion rate [9]. Gasification is a thermochemical conversion technique to convert solid biomass into gaseous mixtures with the help of gasifying agents like air/oxygen, steam and flue gases [10,11]. The gaseous mixture consists of carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), SO<sub>x</sub>, and alkaline gases. Gasification is receiving attention for utilization of biomass stocks, as it provides the liberty to choose different feedstocks [12]. Moreover, it is economical on large scale and has advantages of enhancing clean and green environment and promotion of agro-based culture [13].

Biomass is converted into the gaseous product in the gasifier. The conversion of gaseous products involves many reactions. Reza et al. [12] and Gao et al. [14] discussed the following reactions.

Char gasification reaction	
$C + H_2O \rightarrow CO + H_2$	ΔH=131.5 kJ/mol
Water gas shift reaction	
$\rm CO + H_2O \leftrightarrow \rm CO_2 + H_2$	∆H=−41 kJ/mol
Steam methane reforming	
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	∆H=206 kJ/mol
Boudouard reaction	
$C + CO_2 \rightarrow 2CO$	ΔH=172 kJ/mol

http://dx.doi.org/10.1016/j.rser.2017.01.153

Received 2 November 2015; Received in revised form 20 November 2016; Accepted 25 January 2017 Available online 01 February 2017

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Methanation reaction	
$C + 2H_2 \rightarrow CH_4$	$\Delta H = -74.8 \text{ kJ/mol}$

It is an endothermic process in which biomass is partially oxidized to produce syngas and hydrogen at higher temperatures such as 650-1200 °C. Stefen et al. [15] described the role of gasifying agent. The composition of product gas depends on the type of oxidizing medium used which could be air, pure oxygen, steam, air-steam and oxygen-steam mixtures [13,16]. Steam gasification has advantages over air gasification. Steam gasification is viable for both small and large scale compared to air gasification in terms of less tar production and better product gas composition [17]. Walawender et al. [18] reported that high temperature favoured forward water gas shift reaction and high amount of steam increased hydrogen production and reduced  $CO_2$  formation [18].

The use of catalyst in biomass gasification has undeniable importance as it has an enormous effect on the gas yield [19]. Gas yield is increased by the use of catalyst as evident from the literature that hydrogen yield increased from 33.3 to 52.5 mol% and syngas ratio from 1.15/2.15 to 1.87/4.45 [20,21]. Gasification process produces some unwanted component especially higher hydrocarbons (tar) that not only decrease the yield of product gas but also raise issues of maintenance and operation such as colloguing, deposition and blockage [5]. Catalytic biomass steam gasification received significant attention in the mid-1980s for removal of tar and suppression of unwanted products formation, consequently raising product yield and increasing economic viability of gasification process [22]. The catalyst must be cheaper, self-sustained in strong reaction environment, enhance desired product yield (hydrogen or syngas), potential to reduce tar, capable of hindering sintering and have the catalytic ability that can be restored [23].

The catalyst can be used in two ways; primary and downstream catalyst. Primary catalyst reduces tar formation and enhances the tar reforming into desired product [24]. On the other hand, downstream catalyst provides facility to enhance product yield by accelerating reactions like methane steam reforming, shift gas reaction and char gasification [25]. These are used in different conditions and should have the ability to regain their activity. Basically, there are two types of catalyst used in biomass steam gasification, Mineral based and synthesized catalyst. Mineral based catalyst include dolomite [26], olivine [27,28] and alkaline earth metal [29,30] while synthesized catalyst includes transition metal catalyst for gasification [22,31]. Fig. 1 shows the basic and further classification of catalyst used in biomass steam gasification.

Mineral catalyst contains CaO [32-34], Fe<sub>2</sub>O<sub>3</sub> [27,29,35], oxides of Al [39] and Mg [40,41] and alkaline earth metals [36-38]. All these are used as a catalyst for biomass steam gasification. Coal bottom ash contains oxides of Fe, Ca, Mg, and Al [39-41]. The presence of these compounds shows that it can be used for catalytic biomass steam gasification [42].

Many authors have summarized the role of catalyst in biomass gasification. David Sutton et al. [22] reviewed the literature on biomass gasification till 2000 and briefly discussed the effect of dolomite, alkaline metal and Nickel (Ni) catalysts in the biomass gasification process for different type of gasification agents. In 2003, Devi et al. [43] summarized the published literature on catalysts for tar elimination in biomass gasification. On the other hand, in 2004, Abu et al. [44]

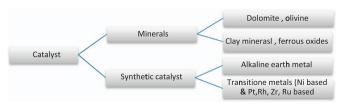


Fig. 1. Types of catalyst used in steam biomass gasification.

described the role of both mineral and synthesized catalyst in tar elimination and discussed the use of catalysts for tar elimination from final product gas perspective [44,43]. In a recent article, Guan et al. [9] discussed the prospect and challenges of catalytic reforming of tar in steam gasification. Catalytic reactions condition is very important in biomass gasification. Yung et al. [45] studied the effect of reaction parameters, catalyst and support material on syngas production.

Hydrogen, an emerging future fuel is a key product of biomass gasification. In 2010, Tanksale et al. [46] summarized the literature on hydrogen production from catalytic biomass gasification. Their study was more focused on process techniques used for hydrogen production via catalytic biomass gasification. With the passage of time, catalysts were modified and promoted with other materials. In 2010, Donald et al. [47] studied the recent advancement in catalyst preparation and their effect on tar reduction in product gas from biomass gasification. In 2014, Chan et al. [4] discussed the recent development in Ni catalyst and their effect on tar reduction and product yield. Recently, Jakkapong et al. [33] reviewed the role of CaO based catalyst for hydrogen production in steam gasification. Shen et al. [48] did a review on recent progress in tar elimination by use of catalyst in biomass gasification.

Based on the critical review, it is observed that biomass steam gasification has a preference to other conventional biomass gasification techniques due to its improved product quality. In recent years, numerous publications have been made on the use of catalyst in steam gasification and it is important to make a brief study of this literature. A lot of work has been done to find new and cheaper catalyst like biomass and coal ashes. The above mentioned reviews did not particularly cover the catalytic effect of steam gasification.

This review is intended to give a better choice to the researcher on the selection of catalyst for steam gasification. The first objective of this study is to summarize the effect of catalysts such as dolomite, alkaline metal and Ni-based catalyst in biomass steam gasification on product yield and tar reduction. The second objective of this review is to provide a detailed overview on the potential of coal bottom ash as a substitute catalyst in steam biomass gasification. This review has a good addition in the state of knowledge with respect to recent development in conventional catalyst and catalytic potential of coal bottom ash.

#### 2. Dolomite catalyst group

Dolomite is an ore of magnesium and calcium with the formula MgCO<sub>3</sub>.CaCO<sub>3</sub>. Its chemical composition depends on ore source and typical compositions are given in Table 1 [26]. Its low price, ease of disposal, and effectiveness in removing tar from product gas has given it prominence as a catalyst [49]. In addition, it has an extra advantage of being used as a primary or downstream catalyst and bed guard material [22].

Dolomite composition has a significant role in tar reduction and product yield. Orit et al. [50] investigated steam/oxygen gasification of wood biomass at a temperature range of 1073-1108 K using different dolomites from Norte, Chinches, Malaga and Seville. These dolomites differ in terms of Fe<sub>2</sub>O<sub>3</sub> content. The result shows that tar conversion is maximum 95% for Norte dolomite and minimum for Seville dolomite about 77%. The Nortel has more Fe<sub>2</sub>O<sub>3</sub> and reactivity than others. This

Table 1	
Composition	of dolomite.

Composition	References
30–35 wt%	Sutton et al. [22]
15-21%	Orio et al. [50]
40-45%	Simel et al. [26]
0-1%	
1-4%	
	30–35 wt% 15–21% 40–45% 0–1%

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