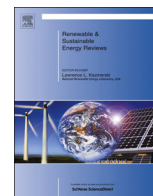




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# Review of recent developments in Ni-based catalysts for biomass gasification



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## ABSTRACT

Biomass gasification is recognized as one of the most promising solutions for renewable energy and environmental sustainability. However, tar formation in gasifier remains as one of the main hurdles that hinder commercialization. Nickel based catalyst is widely used in chemical industries and is proven as one of the most effective transition metal catalysts in biomass gasification for tar cracking and reforming. This paper presents a review of various commercial nickel catalysts that have been evaluated for tar elimination in biomass gasification. This review also looks at recent advancements in nickel based catalyst used in biomass gasification, including discussion on the effects of different support, promoter and particle size on the catalytic performance. Future direction of biomass gasification, including reactive flash volatilization and steam gasification, are also discussed in this review.

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## 1. Introduction

According to the 2011 Energy White Paper by the Australian Department of Resource, Energy and Tourism, the world global energy demand in year 2035 will be 40% higher than current level [1]. However, with the growing concerns about climate change

and greenhouse gas emissions, non-renewable fossil fuels such as coal, petroleum and natural gas can no longer be considered as the only energy sources for the meeting of our future energy needs. In the short to medium term, a versatile and diverse energy plan, comprising both renewable and non-renewable energy sources is required. In the long term, there is a need for global transition to 100% renewable energy and chemical feedstock to achieve sustainable growth.

Biomass is a renewable energy resource derived from biological sources such as energy crops, agricultural residues, forestry

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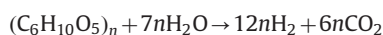
residues and municipal wastes [2]. Biomass utilization is recognized as one of the most promising solutions for our current energy and environmental problems. Alternative renewable energy technologies such as solar energy and wind power, which often suffer from intermittent power generation issue, are less reliable in term of security of supply [3]. Also, biomass is the only renewable energy source that can be converted into liquid fuel and utilized as feedstock in chemicals production [4].

Thermochemical processes for biomass conversion, such as combustion, gasification and pyrolysis, can be used for power generation and biofuels production [5]. Among these processes, biomass gasification has attracted the most attention from both industrial and academic researchers due to its high conversion efficiency [6]. Biomass gasification is a process to convert biomass feedstock into combustible gaseous products like hydrogen, carbon monoxide and methane; however, undesirable products like tar and char are also produced under high temperature and limited oxygen supply environment.

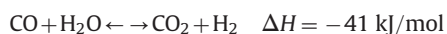
Chemistry of biomass gasification is complex and yet to be fully understood by researchers [7]. It is generally acceptable to say that the major reactions include pyrolysis, oxidation, partial oxidation, reduction, steam reforming and water–gas shift reactions [4,8,9]. Pyrolysis is an endothermic decomposition process which takes place at high temperature in the absence of air or steam. In biomass pyrolysis, the feedstock is converted into gas, liquid tar and solid char products [10] as shown in Fig. 1.

In oxidation or partial oxidation reactions, carbonaceous products from pyrolysis reaction may react further with oxygen to generate more gas and release heat. In the final step of gasification, product gases are upgraded through steam reforming, which converts low molecular weight hydrocarbons such as CH<sub>4</sub> into CO and H<sub>2</sub>. Water–gas shift reaction further converts CO and steam into H<sub>2</sub> and CO<sub>2</sub>. Side reactions such as methanation also occur in gasification but to a lesser extent [11,12]. Using cellulose as a model, the main chemical reactions of biomass gasification can be expressed in the equations below

overall cellulose steam reforming



water–gas shift



methanation



methane steam reforming



Biomass gasification produces condensable heavy hydrocarbons, generally referred to as tar. Tar removal is a major hurdle that hinders the commercialization of the biomass gasification [4]. Accumulation of tar in the gasifier may lead to severe operational problems such as corrosion, clogging and low gasification

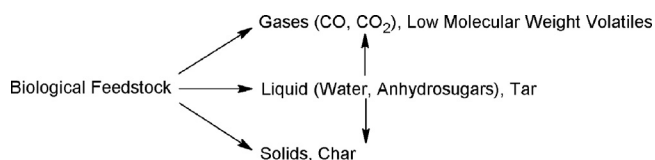


Fig. 1. Pathways for biomass pyrolysis.

efficiency. Recently, significant progress has been made in the gasifier designs coupled with the use of catalysts to overcome these operational problems. The key focus of this paper is to review some of the recent developments in nickel based catalyst used in biomass gasification and tar removal.

## 2. Tar

Tar consists of more than 100 different compounds and is produced in a series of complex thermochemical reactions. The amount of tar produced in biomass gasification is greatly affected by factors such as type of biomass feedstock, particle size, type of gasifier, type of gasifying agent and operating conditions such as temperature and pressure. Table 1 shows an overview of different types of biomass gasification setups. Majority of the gasifiers are operated in a temperature range of 700–1000 °C. Generally, higher operating temperatures lead to lower tar content in the product gas. Among the three designs listed in Table 1, gas product generated from entrained flow gasifier normally has the lowest tar content because they operate at the higher end of the gasification temperature range (1000–1400 °C) [13]. Increasing the pressure of gasifiers also has a positive effect in reducing or eliminating the tar formation [14]. However, it has been observed that increasing the pressure results in greater reduction of light hydrocarbons compared to the heavy hydrocarbons, therefore the fraction of polynuclear aromatic hydrocarbons (PAH) in the tar increases with pressure [15].

In addition to the quantity of tar produced, the composition of tar also depends on the type of biomass feedstock, particle size and gasification conditions used. Fraga et al. [16] showed that the distribution of the furan derivatives in sugarcane bagasse tar was different from the distribution found in silver birch wood tar under the same pyrolysis conditions. Ku et al. demonstrated that the content of PAH found in bamboo pyrolysis tar was higher than the PAH content found in oak and pine wood tar [17]. Furthermore, Qin et al. reported that PAH concentration in tar from sawdust gasification decreased as the gasification temperature increased from 700 °C to 900 °C [18]. Therefore, it is important to understand the composition of tar and the conditions under which different types of tar compounds are formed.

Definition of tar varies widely by study, but it is generally accepted as aromatic hydrocarbons with molecular weight higher than benzene [38]. In order to better understand the characteristics of tar, various ways to classify tar have been suggested. The first approach proposed by Milne et al. [39] divides tar into four groups: primary, secondary, alkyl tertiary and condensed tertiary, based on their experimental results obtained from gas phase thermal cracking reactions. Primary tar, which is defined as low molecular weight oxygenated hydrocarbons, is composed of compounds derived from cellulose, analogous hemicellulose and lignin. Examples of primary tar include levoglucosan and furfurals. Secondary tar is composed of phenolic and olefin compound, including cresol and xylene. Alkyl tertiary tar is composed of methyl derivatives of aromatics such as toluene and the condensed tertiary tar is composed of polynuclear aromatics hydrocarbons (PAH) without the branched molecular groups such as benzene and naphthalene. Alkyl tertiary and condensed tertiary tars are products of condensation reaction of the primary tars at high temperature.

Tar can also be classified based on its components solubility and condensability, as suggested by Kiel et al. [40]. It is crucial to understand the condensability and the solubility of tar compounds because condensation of tar in the reactor may lead to severe operating issues and solubility of tar components may increase the

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