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Biomass gasification gas cleaning for downstream applications: A comparative critical review



Mohammad Asadullah*

Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

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ABSTRACT

Biomass is the only source on earth that can store solar energy in the chemical bond during its growth. This stored energy can be utilized by means of thermochemical conversion of biomass. Gasification is one of the promising thermochemical conversion technologies, which converts biomass to burnable gases, often termed as producer gas. Major components of this gas are hydrogen, carbon monoxide and methane. Depending on the purity, this gas can be used in the furnace for heat generation and in the internal combustion engine and fuel cell for power generation or it can be converted to liquid hydrocarbon fuels and chemicals via the Fischer–Tropsch synthesis method. Despite numerous applications of the biomass gasification gas, it is still under developing stage due to some severe technological challenges. Impurities such as tar, particulate matters and poisonous gases including ammonia, hydrochloric acid and sulfur gases, which are unavoidably produced during gasification, create severe problems in downstream applications. Therefore, the cleaning of producer gas is essential before being utilized. However, the conventional physical filtration is not a technically and environmentally viable process for gasification gas cleaning. The utilization of catalyst for hot gas cleaning is one of the most popular technologies for gas cleaning. The catalyst bed can reform tar molecules to gas on the one hand and destroy or adsorb poisonous gases and particulates on the other hand, so as to produce clean gas. However, numerous criteria need to be considered to select the suitable catalyst for commercial use. In this review, the advantages and disadvantages of different gas cleaning methods are critically discussed and concluded that the catalytic hot gas cleaning with highly efficient catalyst is the most viable options for large-scale production of clean producer gas.

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* Tel.: +60 3 5543 6359; fax: +60 3 5543 6300.

E-mail address: asadullah@salam.uitm.edu.my

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1. Introduction

Biomass is one of the most plentiful organic materials on the earth, which is produced by photosynthesis reaction in green plant in the presence of sunlight. It stores solar energy in its chemical bonds as a chemical energy [1], which can be further evolved by breaking down the bonds [2]. Thermochemical conversions including combustion, gasification and pyrolysis are the processes that can break down the chemical bonds in biomass to release the stored energy. Combustion can directly release the energy by primary bond breaking of biomass, while gasification and pyrolysis can transfer the energy into secondary products (gas and liquid), which are likely to be ideal for fueling the furnace and the engine [3]. Based on the advantages in terms of energy efficiency and ease of application, gasification is the best choice for exploiting energy from biomass [4]. It converts biomass into fuel gas (producer gas), consisting of hydrogen, carbon monoxide, carbon dioxide and nitrogen as major components along with some methane and other minor components. This gas is readily burnable either in the furnace for heat generation or in the internal combustion engine for power generation [5–7]. Since the gas is rich in H₂ and CO, they can be separated to utilize for fuel cell [8,9] or to convert into liquid hydrocarbon fuels or chemicals by the Fischer–Tropsch synthesis method [10,11].

Despite the numerous advantages of biomass gasification, the technology is still in the developing stage due to some challenges. Impurities such as tars, particulate matters, NH₃, H₂S, HCl and SO₂, which are unavoidably produced during gasification and generally sustained in the producer gas, cause severe problems in downstream applications [12–16]. These contaminants must be removed before the gas is being used for internal combustion engine, fuel-cell, and for secondary conversion into liquid fuels or chemicals by Fischer–Tropsch synthesis [8–11]. Among the impurities, tar is the notorious one, which represents a number of organic compounds, especially aromatic compounds heavier than benzene [17–19]. Tar is a sticky material, which usually condenses in the low-temperature zone of the downstream applications and blocks the narrow pipeline. As reported, the tar tolerance limit varies depending on various applications such as ~500 mg/Nm³, ~100 mg/Nm³ and 5 mg/Nm³ and is recommended for compressors, internal combustion systems, and direct-fired industrial gas turbines, respectively [20]. For Fischer–Tropsch synthesis, the tar concentration must be even lower (< 0.1 mg/Nm³) [21,22] along with ammonia concentration < 10 ppm, which is produced generally in the range of 1000–5000 ppm in producer gas, depending on the raw materials and operating conditions used [23]. During gasification, most of the nitrogen content in biomass ends up as NH₃, N₂, HCN and HNCO as well as NO_x [23–26].

The formation of tar and NH₃ is a function of air–fuel ratio as well as process temperature. It is well reported that the higher air to fuel ratio and temperature favor reducing the tar and NH₃ concentration in the producer gas [18,27–29]. However, two problems can be encountered for high-temperature and high

air–fuel ratio. Firstly, high-temperature gasification requires expensive alloy materials for reactor constriction as well as high temperature is very tough to maintain [30,31]. Secondly, the high air to fuel ratio reduces the burnable gas composition in the producer gas [32]. This means that the contaminants must be removed by other means such as physical filtration, wet scrubbing or catalytic hot gas cleaning. The physical filtration is a simple method of tar and particles separation; however, the agglomeration of sticky tar and particles often blocks the pores of filter. In addition, it cannot separate gaseous impurities. The most severe problem of physical filtration and wet scrubbing methods is the handling and disposal of toxic tar. For large-scale gasification of biomass, the stringent environmental regulation does not allow the disposal of such a huge quantity of toxic tar into the environment. Therefore, catalytic hot-gas cleaning could be considered as an attractive option for removing contaminants from the gasification gas. This method is indeed more advantageous in terms of energy efficiency as it eliminates the gas cooling step for physical filtration and the reheating step of gas for downstream application.

Comprehensive researches have been conducted for catalyst development in order to reform tar to gases over the last couple of decades. Tar is a mixture of a wide range of aromatic hydrocarbons and their derivatives. In principle, these aromatic hydrocarbons along with light aliphatic hydrocarbons including methane can undergo reforming or cracking reaction on some catalysts to form gaseous products at certain temperatures [33–37]. At the same time ammonia can also be decomposed on the Fe, Ni and Ru based catalysts [38–41]. However, HCl, H₂S and SO₂ do not decompose on the catalyst; instead they are highly soluble in water, and hence they can be separated by water scrubbing [42].

The reactions involved in catalytic hot gas cleaning are extremely slow due to the inertness of the poly-aromatic compounds, which is usually formed by the recombination of small molecules [43], requiring high temperature and activation energy to start the reaction. In addition, other gaseous impurities especially HCl, H₂S and SO_x can be permanently adsorbed on the active sites of the catalyst, so as to reduce the catalytic activity. Under the reaction conditions, the tar can be readily converted to coke, which in addition to particulate matter builds up on the catalyst surface and covers the active sites, hindering the tar and reforming agents to come into contact with the reaction site. Therefore, it is obvious that catalytic hot gas cleanup requires a highly reactive and resistive catalyst. The catalyst must be highly selective to gas formation route instead of coke formation route. In addition, the catalyst must be able to transfer oxygen to the deposited carbon to clean up the surface by fast oxidation reaction.

Different types of catalysts have been proven to be active for tar and ammonia decomposition. In order to reduce the tar content in the product gas stream, catalysts have been used either in the primary bed or in the secondary bed. In the case of primary bed, the catalyst is placed in the gasification reactor where the biomass is directly fed [44–46]. However, the catalyst is rapidly deactivated due to the fouling of ash and carbon on the surface. Non-metallic catalysts such as dolomite and olivine show longer activity in the

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