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Renewable hydrogen production from bio-oil derivative via catalytic steam reforming: An overview

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ABSTRACT

Tremendous research efforts have been dedicated towards development and utilization of sustainable alternative energy resources. Depletion of fossil fuels and the rising environmental concerns such as global warming are among the reasons that necessitated such. Hydrogen (H_2) has been widely considered a clean fuel for the future, with the highest mass based energy density among known fuels. Bio-oil components are the most renewable energy carriers produced from bio-mass which have been selected for hydrogen production. Phenol and acetic acid are among the major liquid waste components of the bio oil. Catalytic steam reforming of these components in a fixed bed reactor provides a promising technique for hydrogen production from renewable sources. Due to the vital interaction that exists between catalyst and supports, Rh and Ni active metals and ZrO_2, La_2O_3 and CeO_2 supports were found to be appropriate catalysts with long-term stability for the hydrogen production via steam reforming of phenol and acetic acid. The process is advantageous due to its high hydrocarbon conversion and H_2/CO_2 product ratio. The present work provides extensive information about the phenol and acetic acid steam reforming process for producing hydrogen as a renewal energy carrier.

1. Introduction

Exhaust from motor cars has been identified as a one of the major source of pollution and is becoming more unpleasant to the people inhabiting cities [1]. The low emission demands in the automobile industries as well as other pollution problems are the great concern in the 21st century [2]. High efficient vehicles are the simplest key to decreasing emissions [3]. However motor vehicles cause pollution due to a number of reasons, including emissions of NO_x, SO_2 and other particles [4]. Most of this pollution has a health impacts such as irritation in the breathing system, skin and eyes as well as environmental impact such as emissions of greenhouse gases [5]. Even with the continuous economic growth, most progressive industrialized countries have not increased their total energy consumption during the past three decades [6]. Yet, the energy use in transport sector keeps increasing in many parts of the world.

Hydrogen as energy carrier on board for transportation was recognized because of its environmentally friendly nature [7]. The energy density of hydrogen is greater compare to other fuels and its energy yield is 122 kJ/kg. This energy yield is 2.75 times more than other hydrocarbon fuels [8]. Management issues related to the hydrogen as an energy carrier includes its production, transmission, storing and usage [9]. The products of hydrogen combustion is water and can play a significant role in energy systems in the future. Consequently hydrogen is considered as a promising energy product and there has been a surge in funding devoted for research on the production, distribution, storage, and hydrogen use worldwide [10]. Therefore, hydrogen production is a matter of great importance in clean fuel production. The cost for present technology to produce hydrogen is more expensive than fuel which is in used now but production cost could decline if the market increases and knowledge of production is developed [11]. The total price of using the underground facilities for central hydrogen storage could be equal to those of natural gas storage facilities but the hydrogen transmission cost is probable to be to some

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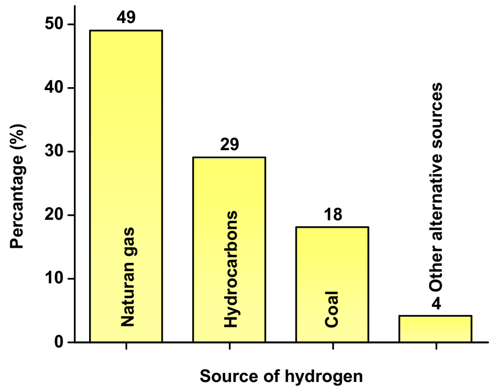

Fig. 1. Several sources of hydrogen production (adapted from Parthasarathy et al. [8]).

extent higher than the natural gas transmission [12].

Currently, hydrogen is industrially produced from the fossil fuel and its production is based on natural resources as it main sources, such as natural gas (mainly) and naphtha [13]. Fig. 1 shows the different sources of hydrogen production. The catalytic steam reforming of natural gas or coal gasification are current well-established hydrogen production methods. These engineering processes cause emission of large quantity of greenhouse gases such as carbon dioxide into atmosphere [14,15]. Due to the release of the greenhouse gases (mainly CO_2) into the environment, its reflected as untenable or unsustainable. Hence the fuel cells, internal combustion engines and other applications of hydrogen could be a noble options for fuels, if it can be produced at high efficiency and made from renewable resources [16].

Pure hydrogen gas does not exist as a natural resource like natural gas and oil. Therefore, hydrogen is extracted from natural resources like water [17], coal gasification [18], natural gas [19], acetic acid [20], glycerol [21,22], butanol [23], ethanol [24], methane [25], naphtha catalytic steam reforming [26] and bio-oil [27]. In order to extract hydrogen from these existing resources, energy must be spent. Bio-oil is renewable and has benefit in the environment and hence preferred as source for hydrogen [28]. Recently, the unwanted and nonfuel component of bio-oil which are acetic acid and phenol, were selected as raw materials for hydrogen production [29–31].

Due to the presence of hydrogen ions, phenol is considers as an acid compound and it can act as a weak acid due to its stability as phenoxide ion [32]. Furthermore, the acidity of bio-oil is not suitable for engine fuel. Its major problems is that it serves as corrosive resistant materials for engine fuel. In order to solve this problem, the phenol in the bio-oil can be separated out and added value in others usage. For example, phenol becomes a source in the catalytic steam reforming (SR) for hydrogen production.

The phenol and acetic acid as a source of hydrogen production are selected because they are the main bio-oil components with up to 38 wt %. [33] and 30 wt%. [34], respectively. Hydrogen production from phenol and acetic acid has attracted a considerable amount of attention, as demonstrated by the number of publications in recent years. Their non-inflammable nature makes them safe hydrogen carriers [33]. They are waste products which are the most representative constituents of the water-soluble fraction of bio-oil. Phenol and acetic acid can get a wide variety of microbes, such as bacteria, fungi and viruses [35]. They are reactive and corrosive compound of pyrolysis oil and are not suitable for the internal combustion due to the problem they cause to the engines. Phenol also can be found anywhere in the industrial wastewater, for example from textiles and pharmaceuticals industry [36,37].

Presently, the source of the production of hydrogen is mainly natural gas at high temperature. Though, the emission of greenhouse gases and environmental pollution are the problems of hydrogen production from natural gases. Consequently, the advantages of using phenol and acetic acid as a source of hydrogen production are their environmental-friendliness as well as being renewable and sustainable sources. Therefore, it would be beneficial for those interested in H_2 production research to get an idea about the current status of this industry, including the chemical processes involved, suitable catalysts, supporting materials, operating conditions for high phenol and acetic acid conversion and hydrogen selectivity. The objective of this paper is to provide an overview of literatures on major catalytic studies for H_2 production by bio-oil derivative components such as phenol and acetic acid steam reforming and make through a comparative analysis.

2. Hydrogen and its application

Hydrogen is found to be an important and most plentiful chemical element in the world [38] and comprising about 75% of the earth's elemental mass [8]. The production of hydrogen involves removing and isolating hydrogen at the purity level required for a particular use in the form of independent molecules. In spite of its simplicity, it is difficult to find hydrogen in its pure form. Generally, it is found in combined with further elements such as oxygen (H_2O), carbon (CH_4) or nitrogen (NH_3). Therefore, we need a process to separate hydrogen from other elements. This can be achieved through some desired reaction processes. Hydrogen can also be separated from hydrocarbons such as, gasoline, natural gas, methanol and propane by using a heat-process (reforming) [39].

2.1. Energy carrier uses

The usage of hydrogen as an energy carrier is on the increase. The low energy density by volume limits these uses of hydrogen. But there are many applications where the density is not a big deal. The advantages of hydrogen as an energy carrier include its low environmental pollution impact and diversity in usage. The possible disadvantage may be the high requirements for sealed containers and pipelines needed to prevent leakage.

2.2. Combustion uses

Hydrogen can be used in motorcars like Otto and Diesel engines as a fuel in engines of conventional spark-ignition. The efficiency of

Table 1
Safety-related properties of hydrogen and other fuels [6].

Property	Hydrogen	Methanol	Methane	Propane	Gasoline	Unit
Minimum ignition energy	0.02	0.14	0.29	0.25	0.24	10^{-3} J
Flame temperature	2045	1910	1875	2800	2200	°C
Auto-ignition temperature in air	585	385	540	510	230–500	°C
Maximum flame velocity	3.46	0.58	0.43	0.47	0.42	m s^{-1}
Range of flammability in air	4–75	7–36	5–15	2.5–93	1.0–7.6	vol%
Diffusion coefficient in air	0.61	0.16	0.20	0.10	0.05	10^{-4} m^2 s^{-1}
Higher heating value	141.9	20.0	55.5	50.2	46.5	kJ/g
Lower heating value	119.9	18.1	50.0	46.3	43.4	kJ/g