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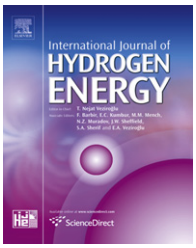

Characteristic of hydrogen and syngas evolution from gasification and pyrolysis of rubber

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ABSTRACT

The characteristics of syngas evolution during pyrolysis and gasification of waste rubber have been investigated. A semi-batch reactor was used for the thermal decomposition of the material under various conditions of pyrolysis and high temperature steam gasification. The results are reported at two different reactor temperatures of 800 and 900 °C and at constant steam gasifying agent flow rate of 7.0 g/min and a fixed sample mass. The characteristics of syngas were evaluated in terms of syngas flow rate, hydrogen flow rate, syngas yield, hydrogen yield and energy yield. Gasification resulted in 500% increase in hydrogen yield as compared to pyrolysis at 800 °C. However, at 900 °C the increase in hydrogen was more than 700% as compared to pyrolysis. For pyrolysis conditions, increase in reactor temperature from 800 to 900 °C resulted in 64% increase in hydrogen yield while for gasification conditions a 124% increase in hydrogen yield was obtained. Results of syngas yield, hydrogen yield and energy yield from the rubber sample are evaluated with that obtained from woody biomass samples, namely hard wood and wood chips. Rubber gasification yielded more energy at the 900 °C as compared to biomass feedstock samples. However, less syngas and less hydrogen were obtained from rubber than the biomass samples at both the temperatures reported here.

1. Introduction

Exploring greater use of renewable energy sources is of pinnacle importance especially with the limited reserves of fossil fuels. Therefore, one must determine means to harvest energy from waste materials, including materials that are not bio-degradable. It is also critical to develop renewable energy sources that are carbon neutral or carbon negative so as to reduce the amounts of greenhouse gas emissions to the environment. With our quest to develop increased utilization of renewable energy resources, it is expected that future energy use will have increased portfolio of different energy sources mixes in the industrial sector that will include biomass, municipal solid wastes, industrial wastes, agricultural wastes and other low grade fuels as well as high energy density materials such as rubber and plastics. Clean and efficient energy utilization from the various energy mix scenarios will be of paramount importance, in particular for energy sustainability and energy availability.

Development of sustainable renewable energy technologies for their use in current and new power plants is of greater importance now than ever before due to several reasons. Some of these reasons include energy security and availability, independency from foreign oil imports, limited energy resources, and reduction of greenhouse gas emissions to provide cleaner environment for better health, plant and animal life, aesthetics and nature preservation. These reasons encourage research and development engineers to develop alternative

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and sustainable energy technologies for use in current engines without any compromise on the engine performance. Gasification and pyrolysis provide part of the solution for clean harvesting of energy from both low grade and renewable fuels and high energy density wastes of rubber and plastics for energy sustainability and energy security [1–3].

Rubber containing wastes causes a big environmental problem because it is an artificial polymer and is not biodegradable. However, it can be photo degradable but it takes significantly longer time as compared to biomass materials. It takes a very long time for rubber before being digested by the bacteria in landfills. Even then it is not fully bio-degradable but rather becomes brittle material so that the actual material characteristics still remain for decades, if not over millennium.

Rubber and tires represent an important source of renewable energy. Automobile tires alone are big problems not only in the USA but many countries worldwide. It is estimated that about 2 billion tires lie as trash in the USA and additional amounts worldwide. In addition over 200 million tires are added annually in the USA as wastes. Plastics represent an important growing waste problem worldwide. The dumped tires are a big health issue as it attracts mosquitoes, rats and other mammals to create their nests. This in turn causes diseases and other subsequent health issues. In addition to tires plastics is a growing social and environmental problem in the society today. It is estimated that about 80–90% of the plastics is disposed off improperly. The use of plastics in the cars has increase significantly over the years. For example in 1980 average amount of plastics in cars was 86 kg/vehicle, while in 1991 it was 163 kg/vehicle. The use of plastics is expected to increase in the future not only in cars in the transportation sector but also in other applications, such as appliances, toys and selected industrial and consumer applications.

Gasification provides good solution to the problem of clean energy recovery from tires. Beside the gasification has the advantage of complete destruction of different types of materials present in the waste, including tires and rubber, provides energy recovery from such wastes. The residues remaining are minimal. Residues remaining are mainly ash. Ash is not destructed by gasification or combustion. The ash remaining after the gasification process is a valuable product. For example, it can be used in the production of cement and other construction materials. The emission of hazardous pollutants is also eliminated or minimized. For example; NO_x formation is eliminated if steam and/or oxygen are used as gasifying agents. NO_x formation is also minimized even if air is used as the gasifying agent due to the lower reactor temperature as compared to that encountered in direct combustion of waste materials. Note that our gasification temperatures are much lower than the temperatures at which thermal NO_x is formed (1800 °C). Such high temperatures are common in combustion systems that have stoichiometric mixtures at selected regions of combustion chamber but not in the gasification studies conducted here. However, air gasification systems, runs on very rich equivalence ratios and the gasification temperatures are much lower.

In case of rubber, the advantage of gasification is maximized, since rubber has high energy content on both mass and volume basis. Rubber heating value is approximately 37.2 MJ/kg, which is close to the average heating value of plastic (~40 MJ/kg). The heating value of rubber (and also plastics) is significantly higher than that of the biomass, which is only about 18 MJ/kg.

The gasification of rubber has been investigated here with specific focus on the evolution of syngas flow rate, hydrogen flow rate in the syngas, amounts of syngas yield, hydrogen yield and energy yield from a given amount of material. Results of syngas characteristics obtained from the gasification process have been compared to that obtained from the pyrolysis. The comparison was conducted at two reactor temperatures of 800 and 900 °C. Focus on high temperature gasification was due to its unique advantages of high conversion efficiency and reduced amounts of char and tar from the process. The characteristics of syngas from rubber gasification have been compared to that from woody biomass samples, namely hard wood and wood chips. The comparison was conducted for the syngas quality under identical gasification conditions and evaluated in terms of total syngas yield, hydrogen yield, energy yield and hydrocarbons yield.

Several researchers have investigated the kinetics of weight loss of rubber containing samples [4–6]. The results reveal that the kinetics of rubber gasification can be described using parallel first order independent reactions. The results obtained on activation energies depended on the heating rate and the range of investigated temperatures. The activation energy value ranged from 40 to 210 kJ/mol.

Castaldi et al. [7] proposed a reaction mechanism of Styrene–Butadiene Rubber (SBR) decomposition under pyrolysis conditions. The mechanism suggested was based on simultaneous thermogravimetric analyzer (TGA) and gas chromatograph/mass spectrometer (GC/MS) measurements. These investigators have suggested the following decomposition steps for SBR; first, there is a breakage between the ligand and butadiene backbone, which results in some hydrogen liberation. The backbone continues to be hydrogenated to form butane and n-butane. The styrene ligand undergoes various transformations, hydrogenation and removal of methylene groups, leading to the substituted polycyclic aromatic hydrocarbons (PAHs), such as, ethyl-benzene and toluene.

Several researchers have investigated the porosity of char obtained from rubber pyrolysis. San Miguel et al. [8] found that char obtained from pyrolysis of scrap tires developed poor porosity and limited internal pores surface area. On the other hand, Helleur et al. [9] concluded that the poor porosity of the obtained char was enhanced by further carbonization using steam and CO_2 activation. Using steam at 900 °C for 3 h produced an activated carbon with good surface area (302 m^2/g). Steam was observed to generate a narrower but more extensive micro-porosity than carbon dioxide [10,11]. On the other hand, Vizuete et al. [12] concluded that chemical treatment of residual rubber using HNO_3 resulted in large pore structure in the material.

In most of the previous studies not much attention has been paid to the characteristics of syngas evolution from the gasification of rubber containing materials. This is important since rubber possesses high heating value and waste rubber can be used to produce good quality of syngas with high hydrogen content which can then be used in many power and propulsion applications.

In this paper, experimental results are reported on the high temperature steam gasification of rubber. The results from