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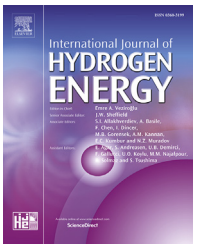

Investigation of a novel & integrated simulation model for hydrogen production from lignocellulosic biomass

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ABSTRACT

Process simulation and modeling works are very important to determine novel design and operation conditions. In this study; hydrogen production from synthesis gas obtained by gasification of lignocellulosic biomass is investigated. The main motivation of this work is to understand how biomass is converted to hydrogen rich synthesis gas and its environmentally friendly impact. Hydrogen market development in several energy production units such as fuel cells is another motivation to realize these kinds of activities. The initial results can help to contribute to the literature and widen our experience on utilization of the CO_2 neutral biomass sources and gasification technology which can develop the design of hydrogen production processes. The raw syngas is obtained via staged gasification of biomass, using bubbling fluidized bed technology with secondary agents; then it is cleaned, its hydrocarbon content is reformed, CO content is shifted (WGS) and finally H_2 content is separated by the PSA (Pressure Swing Adsorption) unit. According to the preliminary results of the ASPEN HYSYS conceptual process simulation model; the composition of hydrogen rich gas (0.62% H_2O, 38.83% H_2, 1.65% CO, 26.13% CO_2, 0.08% CH_4, and 32.69% N_2) has been determined. The first simulation results show that the hydrogen purity of the product gas after PSA unit is 99.999% approximately. The mass lower heating value (LHV_{mass}) of the product gas before PSA unit is expected to be about 4500 kJ/kg and the overall fuel processor efficiency has been calculated as ~93%.

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Nomenclature

Abbreviations

PSA	Pressure swing adsorption
WGS	Water gas shift
PFD	Process flow diagram
E	Heat exchanger
RQE	EQ-R Equilibrium reactor
STD	Standard
FP_{Ef}	Fuel processor efficiency
CG_{Eff}	Cold gas efficiency
LHV_{mass}	Mass lower heating value
HHV	Higher Heating Value

Symbols

F	Feed
P	Pressure
T	Temperature
W	Water
ΔH°	Formation enthalpy
Q	Heat flow

Introduction

Terrestrial biomass is a renewable, widespread and abundant energy source which captures carbon dioxide $(CO_2)_g$ that leads to the green-house effect in the atmosphere, through photosynthesis and keeps it within the carbon cycle.

Finite nature of conventional fossil fuels, climatic concerns, and eco health issues related to their utilization render biomass an alternative route to hydrogen, a critical energy carrier [1–6]. As a renewable resource, contribution of biomass to the world energy demand is approximately 10–14% [4]. Gasification is the optimum and most economic approach for usefully eliminating biomass originating from forest and agricultural residues without environmental hazard [7]. Hydrogen can be obtained by thermal gasification of biomass. The hydrogen content of biomass is approximately 6–6.5% by weight and the average hydrogen yield is 63% [8]. Hydrogen produced via biomass gasification is presently more expensive than conventional hydrogen from steam methane reforming [9].

Lignocellulosic biomass wastes are defined as a renewable energy source. It is very important to evaluate the potential energy of these sources. There are some existing works done by several countries in the world. These sources have also been utilized as a fuel and energy material within some countrified areas of Turkey.

Solid biomass resources, a great majority of which are lignocellulosic, can be converted into gaseous fuels through thermochemical gasification processes. A gasification process involves successive drying, pyrolysis and gasification steps in the reactor. During the gasification step, many chain reactions take place. The resulting "product gas", mainly contains hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and nitrogen (N_2). The product gas also contains particulates, tar (Topping Atmosphere Residue), ammonia (NH_3) and sulfur compounds in minor amounts depending on the operating conditions. After passing the product gas through cleaning, reforming and shift processes, "synthesis gas", which is composed of CO and H_2 is obtained; and following separation stage, pure hydrogen gas is produced.

Basic gasification reactions are given in Table 1.

The "product gas" can be used only after processing and obtaining "synthesis gas" composed of CO, CO_2 and H_2. Synthesis gas, in which H_2/CO ratio can be regulated, is widely used in industrial applications such as the Fischer-Tropsch process, methanol synthesis and ammonia production [11]. Carbon monoxide is converted to carbon dioxide through the catalytic water gas shift (WGS) reaction (Table 1).

In most hydrocarbon processors, the water gas shift reactor is the biggest and heaviest component because the reaction is relatively slow compared to the other reactions and is inhibited at higher temperatures by thermodynamics [12].

Water gas shift reaction is the intermediate step used for hydrogen enrichment and CO reduction in the synthesis gas. Water gas shift reaction is a moderately exothermic reversible reaction. The equilibrium constant of the reaction decreases with increasing temperature. The reaction is thermodynamically favored at low temperatures and kinetically favored at high temperatures. Since there is no change in the volume from reactants to products, the reaction is not affected by pressure. The WGSR can be catalyzed by both metals and metal oxides [13].

The WGS reaction is reversible and exothermic ($\Delta H^{\circ} = -41.2$ kJ/mol). Due to its moderate exothermicity, the WGS reaction is thermodynamically unfavorable at elevated temperatures. This is illustrated by the continuous decline and eventual sign change in the Gibbs free energy as a function of temperature, and the corresponding decreasing equilibrium constant as temperature increases. The kinetics of the catalytic reaction is more favorable at higher temperatures [14].

Catalysts containing oxides of iron, copper and nickel; and sulfides of cobalt and molybdenum are generally used in WGS. Hydrogen can be easily separated from mixtures with CH_4, CO, CO_2 and N_2 via adsorptive processes, owing to its low physical

Table 1 – Basic gasification reactions [10].

Char combustion
$C + 1/2\ O_2 \rightarrow CO$ (Partial oxidation)
$C + O_2 \rightarrow CO_2$ (Oxidation)
Char Gasification
$C + CO_2 \rightarrow 2CO$ (Boudard)
$C + H_2O \rightarrow CO + H_2$ (Primary WGS[a])
$C + 2H_2O \rightarrow CO_2 + 2H_2$ (Secondary WGS[a])
$C + 2H_2 \rightarrow CH_4$ (Methanation)
Oxidation of volatile matter
$CO + 1/2\ O_2 \rightarrow CO_2$ *(Partial oxidation)*
$H_2 + 1/2\ O_2 \rightarrow H_2O$ *(Oxidation)*
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2H_2O$ *(Oxidation)*
$CO + H_2O \rightarrow CO_2 + H_2$ *(WGS[a])*

[a] Water Gas Shift reaction

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