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Catalytic steam gasification of pinewood and eucalyptus sawdust using reactive flash volatilization

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ABSTRACT

Catalytic steam gasification of cellulose using reactive flash volatilisation (RFV) has been proven as a promising approach for syngas production. However, using cellulose as feedstock is economically unfavourable. This paper investigates the production of syngas using RFV of pinewood and eucalyptus sawdust as feedstock. Experiments were conducted to evaluate the effects of catalyst promoters, carbon to oxygen ratio, carbon to steam ratio, feedstock type and ash contents on product yields (i.e. gas, tar and char) and product gas composition. High gasification efficiency and low char selectivity were observed in the pinewood RFV with Re-Ni and Rh-Ni catalysts, which can be explained by the catalysts high active metal substrate dispersion. Additionally, in comparison to cellulose, higher gasification efficiencies were also observed in the pinewood and eucalyptus RFV. This can be attributed to the effects resulted from higher amorphous structure of lignocellulosic biomass compared to microcrystalline cellulose, and the catalytic effects of alkali and alkaline earth metals (AAEM species) found in the lignocellulosic biomass ash. The catalytic effects o f AAEM species further reduced the coke deposition on the Ni catalysts, making the effect of noble metal promoter on the Ni catalysts less significant. The effects on product yields and gas composition from promoters, carbon to oxygen ratio and carbon to steam ratio were less pronounced.

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1. Introduction

With the growing concerns on climate change and greenhouse gas emissions, there is an urgent need for global transition from fossil based energy sources to renewable energy sources. Lignocellulosic biomass, as a renewable and carbon neutral energy source, is recognized as one of the most promising solutions for this issue due to its wide availability. Lignocellulosic biomass is the most abundant renewable biomass which has an estimated annual production of 10 billion MT [1].

There are a number of conversion technologies for utilizing biomass as renewable energy resource, such as thermal conversion (combustion), biochemical conversion (anaerobic digestion and fermentation), agrochemical conversion (oil extraction) and thermochemical conversion (pyrolysis, gasification, liquefaction, etc.) [2]. Among all the processing technologies, thermochemical biomass gasification receives the most interests from both industrial and academic researchers because of its high conversion efficiency and feedstock flexibility [3,4]. Synthesis gas can be produced via conventional biomass gasification in fluidised bed reactors at moderate temperatures, usually >700 °C. However, the product gas, in most cases, contains high concentration of undesired by-products such as tar and soot, which makes it unsuitable for use in downstream applications such as fuel cell [5]. Furthermore, accumulation of tar in the reactor may also lead to severe operational issues such as corrosion and clogging. Generally, downstream conversion of char and tar is necessary for the clean-up of synthesis gas.

Our previous publication demonstrated that clean synthesis gas can be produced via reactive flash volatilization (RFV) over nickel based catalysts using cellulose as the feedstock [6]. RFV is a complex process which involves pyrolysis, partial oxidation, steam reforming and water gas shift reactions. With carbon space velocity and carbon mass flow rate of 10–100 times higher than conventional fluidised bed reactors, tar free synthesis gas can be produced in a single fixed bed reactor allowing a short residence time of less than 50 ms. However, it is economically unfavourable to use microcrystalline cellulose as feedstock because biomass pre-treatment represents one of the most expensive steps in the processing of lignocellulosic biomass. In fact, the capital investment cost and operating cost of biomass pre-treatment process for a bioethanol production plant can be as high as 19% of the total capital expenditure and 32–38% of the total operating expenditure, respectively [7,8]. Therefore, it is more cost effective to use whole lignocellu-

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losic biomass such as pinewood and eucalyptus wood waste with minimal pre-treatment.

In addition, it has been widely reported that catalytic effects from the inherent alkali and alkaline earth metals (AAEM species) in raw biomass can be beneficial to the gasification process as it accelerates the conversion of biochar and leads to higher gaseous product yield [9–13].

Therefore, in the present work, RFV of untreated pinewood and eucalyptus sawdust over promoted nickel based catalysts were investigated. The focus of this study was to evaluate the effects of carbon to oxygen (C/O), carbon to steam (C/S) ratio, biomass feedstock and inherent alkali and alkaline earth metals species (AAEM species) on product yields.

2. Experimental

2.1. Biomass

Softwood (pinus radiata, referred to as pinewood henceforth, 550 μm) and hardwood (eucalyptus regnans, referred to as eucalyptus henceforth, 500 μm), obtained from Pollard's Sawdust Supplies, Victoria, Australia, were used as feedstock in this investigation.

2.2. Biomass characterization

Physical and chemical properties of the biomass were characterized according to the European Standards (EN) or Australian Standards (AS). Moisture content of the biomass was determined according to EN14774. Ash yield was determined according to EN14775. Volatile matter, carbon, hydrogen and nitrogen content were determined according to EN15148:2009. Sulphur was determined according to AS1038.6.3.3.

Elemental analysis of the alkali and alkaline earth metals in biomass was performed using an Ametek Spectro iQ II X-Ray Florescence (XRF) Spectrometer. Biomass ashing was carried out by heating 25 g of the sample in air at 600 °C for 6 h. Ash residue was then recovered and subjected to XRF elemental analysis.

2.3. Catalyst

Three nickel based catalysts: Ru-Ni, Rh-Ni and Re-Ni supported on γ-alumina were developed using wet impregnation method. These bimetallic catalysts had nickel content of 10 wt% and noble metal promoter content of 1 wt%. Detailed synthesis procedures and characterizations of these catalysts can be found in our previous publication [6].

2.4. Reactor setup

Catalytic activity evaluation was conducted in a bench-scale reactor setup. Detailed description of the setup can be found in our previous publication [6].

Approximately 1 g of the promoted nickel catalyst was loaded onto fritted disc mounted at the centre of a 25 mm OD, 700 mm long quartz reactor before housed in an electric furnace. Prior to

Table 1
Physical and Chemical properties of Pinewood and Eucalyptus Sawdust.

	Pinewood Sawdust	Eucalyptus Sawdust
Properties		
Acidity (pH)	3.5–4.6	Not Available
Colour	cream to light brown	light to dark brown
Density	12–18 pounds/cubic feet	Not Available
Solubility in water	<0.1%	highly insoluble
Specific Gravity	0.5–0.8	Not Available
Particle Size	<550 micron	<500 micron
Proximate analysis (% db)		
Moisture Content,% ar (EN14774)	7.70	9.80
Ash Yield (EN14775)	0.80	7.30
Volatile	84.1	76.6
Fixed Carbon	15.1	16.0
Ultimate analysis (% db)		
Carbon	50.1	47.3
Hydrogen	6.20	5.30
Nitrogen	0.12	0.14
Sulphur	0.03	0.04
Oxygen[a]	42.8	39.9
Ash analysis (%)		
MgO	30.95	33.08
Al_2O_3	2.59	6.73
SiO_2	3.40	26.1
P_2O_5	11.27	3.20
SO_3	6.51	5.11
Cl	3.30	6.95
K_2O	22.35	4.14
CaO	17.55	11.33
TiO_2	0.12	0.46
V_2O_5	Not Available	0.05
Cr_2O_3	0.04	0.12
MnO	1.19	0.48
Fe_2O_3	0.38	1.97
CoO	0.09	0.10
NiO	0.06	0.01
CuO	0.01	0.02
ZnO	0.09	0.05
Ga	0.01	Not Available

[a] Calculated by difference.