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Hydrogen-rich gas production from algae-biomass by low temperature catalytic gasification

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ABSTRACT

H_2 rich gas produced from *Scenedesmus almeriensis* biomass residue after lipidic extraction by low temperature catalytic gasification is addressed. The pyrolysis–gasification behavior under different atmospheres (CO_2/He, H_2O/He and $CO_2 + H_2O$/He) were investigated using thermal gravimetric analysis. The conversion of the biomass takes place into three stages, according to its composition and corresponding to: loose of water bonded (30–200 °C), major pyrolysis involving devolatilization (200–500 °C) and decomposition of bio-char produced (500–800 °C). The calculated apparent activation energy for the main pyrolysis stage was 97 kJ mol^{-1}. Ni-based supported alumina catalysts (Ni, Ni–Pt and Ni–Rh) were prepared by impregnation. The catalyst influence on the final gas composition as well as in its HHV determined in mixed $CO_2 + H_2O$/He gasification carried out in a double fixed bed reactor configuration with the catalyst located in the second bed upstream. Parallel and secondary reactions as reforming of tar and char together with WGS and Boudouard also take place favoring gas fraction yield with a value close to 0.3 Nm^3 of gas per kg of biomass. The catalytic role of Ni–Pt/Al_2O_3 catalyst in further reforming of the gas resulting from the gasification improves H_2 content even at low temperature interval (600–700 °C).

1. Introduction

The conversion of microalgae biomass to energy and valuable chemicals are gaining significant attention over the last few years. Considering a very high photosynthetic effectiveness, a fast rate biomass growth even under nutrients limitations, the resistance to various types of contaminants, the capacity of making changes in the metabolic routes favoring different final biomass composition and the possibility of land management that cannot be used for other purpose, microalgae appears as a competition to typical energetic crops [1–4]. Most of research works published so far have been focused on the biodiesel production technologies based on lipids that are accumulated in large quantities in cells of algae [5]. In contrast, the use of microalgae as potential substrates in processes of biogas production has recently been addressed.

Biomass-to-fuel (liquid or gas) conversion technologies can be classified into two categories, namely biochemical and thermochemical [6]. Thermochemical technologies utilize high temperature and or catalysts to produce char, oil and gas. There are two major thermochemical reaction pathways: gasification and pyrolysis. Pyrolysis processes also heat biomass in the absence of oxygen, but at a relatively lower temperature (450–600 °C). The main product of the pyrolysis process is a crude-like liquid known as pyrolysis oil, while gas and charcoal are also produced. Depending on the length of the reaction time, there are slow pyrolysis, intermediate pyrolysis, and fast pyrolysis. Fast pyrolysis is often adopted because the yield of pyrolysis oil is maximized [7]. In the gasification pathway, the biomass resources are fed into a gasifier, where they are thermally decomposed with limited or no oxygen, and then oxidized to yield a raw syngas, which is primarily a mixture of hydrogen and carbon monoxide.

Several researches have been conducted on biomass gasification [8] for improving the producer gas composition (H_2, CO, CO_2, CH_4 and C_nH_m), obtaining a gas with considerable LHV, reducing the tar and char content of the effluent stream and enhancing the gas yield, cold gas efficiency and carbon conversion. It is very difficult to meet all these performance indexes at their desirable values at the same time, for example, increasing the bed temperature to reduce the tar concentration will significantly reduce the LHV and cold gas efficiency. The main reactions taking place during the conversion

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Table 1
Main gasification reaction.

	ΔH_r° (kJ mol^{-1})	
Devolatilization		
Biomass + Q → Carbonaceous residue (char) + tars + oils + gases (CO, CO_2, H_2, CH_4, C_nH_m)	Endothermic	(1)
Secondary cracking and reforming	Endothermic	
Tars + $H_2O \leftrightarrow CO, H_2$		(2)
Tars + Q → char + gases (CH_4, H_2, C_nH_m)		(3)
Combustion		
$C + O_2 \rightarrow CO_2$	−394	(4)
$C + 1/2O_2 \rightarrow CO$	−123	(5)
$CO + 1/2O_2 \rightarrow CO_2$	−283	(6)
$H_2 + 1/2O_2 \rightarrow H_2O$	−242	(7)
Gasification		
Char gasification		
$C + H_2O \rightarrow CO + H_2$, Water gas reaction	131	(8)
$C + CO_2 \rightarrow 2CO$, Boudouard reaction	171	(9)
Water gas shift reaction (WGS)		
$CO + H_2O \leftrightarrow CO_2 + H_2$	−41	(10)
Hydrocarbons reforming reactions	Endothermic	
$C_nH_m + nCO_2 \rightarrow m/2H_2 + 2nCO$		(11)
$C_nH_m + nH_2O \rightarrow nCO + (m/2 + n)H_2$		(12)
Methanations		
$CO_2 + 4H_2 \rightarrow CH_4 + H_2O$	−165	(13)
$CO + H_2 \leftrightarrow CH_4 + H_2O$	−205	(14)
Cracking reactions		
$C_nH_m + (2n - m/2)H_2 \rightarrow nCH_4$	Exothermic	(15)

process are covered in Table 1 [9,10]. The presence of catalyst in the bed material during biomass gasification promotes several chemical reactions which affect the composition and heating value of the producer gas. It also reduces the tar yield and prevents solid agglomeration tendency of the bed [11]. Ni or Co based catalysts that are used for methane and other higher hydrocarbons reforming reaction facilitate the cracking of the biomass heavy fractions, reducing tar formation. In addition, 700–800 °C are required to promote CO and H_2 formation [12,13].

A cheaper, long life and sulphur-resistant material is desirable. In addition, most commercial Ni catalysts present a moderate to rapid deactivation due to surface carbon deposition originated from gasification and/or reforming reaction [14]. Noble metal catalysts (Rh or Pt) showed lower deactivation as well as superior catalytic activity in the conversion of almost all the tar and char at unusually low temperatures (500–700 °C) [15] but their costs are elevated. This paper presents the results of the low temperature catalytic gasification of *Scenedesmus almeriensis* biomass after lipids extraction (*Sc*). In this study, the pyrolysis of the *Sc* in different atmosphere was studied by ATD-TG-MS and a two-stage technology: pyrolysis and gasification processes were conducted in a doubled-fixed bed reactor, under non isothermal and isothermal regime using $CO_2 + H_2O$/He and Ni-noble metal supported catalysts.

2. Experimental

2.1. Biomass characterization

The microalga *S. almeriensis* (*Sc*) was supplied by the FYBOA Investigation Group from the Department of Ecology of the University of Malaga as a dry green powder with particle size <250 μm. Biomass was obtained after lipid extraction in a conventional Soxhlet extraction equipment using hexane as solvent. Proximate and ultimate analyses were performed to determine the composition of the biomass. The elemental compositions (C, H, N, O and S) of the biomass after lipids extraction, tarry substances and char were determined with an *Elemental Analyzer Perkin-Elmer 2400 CHN*. Higher heating value (HHV) was also calculated according to Mahinpey et al. [16], based on the elemental analysis. Proximate analysis included measurement of moisture content, volatile matter, fixed carbon and ash. The moisture content of the biomass was determined by drying the samples in a furnace at 105 °C until no further weight change was observed. The volatile matter measuring was performed in *T.A. Instrument SDT Q600* thermal analyzer. Ash content was carried out according to Sluiter et al. [17]. Fixed carbon content was calculated by different the percentages of volatile matter, moisture content and ash to 100%. The content of lipid was determined by gravimetry. Total protein was determined according to the procedure of Kebelman et al. [18]. The results of proximate, compositional and elemental analysis of *Sc* biomass are shown in Table 2.

2.2. Catalysts preparation

Monometallic Ni/Al_2O_3 and bimetallic $Pt–Ni/Al_2O_3$ and $Rh–Ni/Al_2O_3$ catalysts were prepared by simultaneous incipient wetness impregnation of the support with aqueous solutions of $Ni(NO_3)_2{\cdot}6H_2O$, $Pt(NH_3)_2(NO_2)_2$ or $Rh(H_2O)(OH)_{3-y}(NO_3)_y$ (y = 2–3) as precursors of Ni, Pt or Rh, respectively. In detail, monometallic Ni (4 at nm^{-2}; $4Ni/Al_2O_3$), as well as bimetallic noble metal–Ni catalysts with 4 at nm^{-2} of Ni and a low amount of Pt (0.4 at nm^{-2}; $0.4Pt–4Ni/Al_2O_3$) or Rh (0.04 at nm^{-2}; $0.04Rh–4Ni/Al_2O_3$) were prepared. After impregnation the catalysts were kept in stagnant air at 383 K overnight and then treated in air at 1073 K for 2 h (10 K min^{-1}). A synthesized nanofibrous γ-Al_2O_3 was employed as support (A_{BET} = 100 m^2 g^{-1} and V_P = 1 cm^3 g^{-1}), the synthesis procedure and characterization has been already reported in [19,20]. The synthesized catalysts, Ni, Pt or Rh content and their identification are summarized in Table 3.

The physico/chemical properties of fresh Ni/Al_2O_3, $Ni–Pt/Al_2O_3$ and $Ni–Rh/Al_2O_3$ catalyst were well characterized by various characterization methods, which could be found in our previous studies [20,21]. We stated that in the fresh catalytic systems, the presence of noble metal (Rh or Pt) even in very low loadings inhibits the migration of part of the Ni to form $NiAl_2O_4$, enhancing the Ni accessible sites. A strong noble metal–Ni interaction was also reported that stabilizes the Ni species, promoting its reducibility and the better dispersion of Ni. We have also investigated coke deposition over $Pt–Ni/Al_2O_3$ and $Rh–Ni/Al_2O_3$ (with low noble metal loadings) in mixed ($CO_2 + H_2O$) methane reforming compared to Ni/Al_2O_3 catalysts. It was also been informed the formation of PtNi alloy which the surface enriched in Pt. Low amounts of Pt or Rh in Ni-based catalysts allow an improvement in the reaction stability as well as in the selectivity toward H_2 and CO instead toward coke.

2.3. Reactivity

2.3.1. Thermogravimetric-MS analysis

The study of the pyrolysis–gasification of *Sc* biomass was firstly carried out in a TGA system (*T.A. Instrument SDT Q600*). Samples consisting of 10 mg of biomass and silicon carbide or biomass and catalyst (9/1 wt.) loaded into an alumina crucible were heated from 30 to 800 °C with a heating rate of 10 K min^{-1} under 20% gasifying agent/He atmosphere. H_2O, CO_2 or $H_2O + CO_2$ were used as gasifying agent. Water vapor (1%, v/v) was generated by saturation of carrier gas at 9 °C. A mass spectrometer (QMS 200 Pfeiffer Vacuum Prisma^{TM}) was coupled to analyze the gas products distribution. All wirings were properly thermally insulated to avoid condensation of flue gasses. The m/z signals of H_2 (2), CH_4 (15), H_2O (18),