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Chemical looping steam reforming of acetic acid in a packed bed reactor

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ABSTRACT

Chemical looping steam reforming of acetic acid (CLSR-HAc) was carried out in a packed bed reactor at 650 °C and 1 atm using two nickel-based catalysts ('A' with alumina support and 'B' with calcium aluminate support) to study the effect of the temperature of oxidation (T_{OX}) on the efficiency of the process and the materials properties of the catalysts upon cycling. CLSR-HAc could not be sustained with steady outputs with T_{OX} of 600 °C for catalyst A, but it was conducted successfully at temperatures up to 800 °C, whereas with B it could be operated reaching close to equilibrium conditions over five cycles with T_{OX} of 600 °C. CLSR-HAc can run efficiently for further cycles at the right operating conditions (S/C of 3, WHSV of 2.5 h^{-1}, T_{OX} 800 °C, T_{SR} 650 °C) even in the presence of the side reactions of acetic acid decomposition and coking. The yield of hydrogen produced had a minimum efficiency of 89% compared to equilibrium values, and the acetic acid conversion was in excess of 95% across 10 chemical looping steam reforming cycles. High purity hydrogen (> 90% compared to equilibrium values) was also produced in this study. Chemigrams obtained from TGA-FTIR analysis indicates that two forms of carbon were formed on the catalyst during CLSR-HAc; TEM images and diffraction patterns indicate that poly graphitic carbon and amorphous carbon were formed while SEM images of the oxidised catalyst showed that the carbon was eliminated during the oxidation step of CLSR. A full carbon elemental balance of the process confers that majority of the carbon share (ca 90%) was utilised for efficient steam reforming of acetic acid with ca 10% of the carbon input deposited during the reduction step and subsequently burned during oxidation over the CLSR cycles.

1. Introduction

Hydrogen is a gas utilised in many industries globally; it has a global market share of over 40 million dollars which is expected to increase exponentially to over 180 billion dollars as its demand increases [1]. The significant increase in its demand is notably due to its high utilisation in industrial applications particularly fertiliser industries, oil refining and petrochemical industries, food processing, metallurgical processes [1–3], and increasingly due to the growth of fuel cell technologies. The environmental benefits in regards to its low carbon footprint when utilised potentially as an energy vector are mitigated by the fact that 96% of hydrogen consumed globally is produced from conventional fossil fuels which has prompted vast research on the utilisation of renewable resources for the production of hydrogen.

Biomass resources for H_2 production have advantages over intermittent renewables like wind and solar in that they are abundant globally, provide a natural storage medium, and because they can be harnessed easily [4–6]. The production of hydrogen from biomass can be done through different routes, however; a promising route is an indirect method which involves the fast pyrolysis of the biomass residue to bio-oil first before its conversion to hydrogen [7]. This method offers advantages to direct gasification methods on several fronts. Firstly, unlike many gasification processes, pyrolysis avoids the formation of heavy tars and thus can have a lower burden of clean-up and maintenance. Secondly, pyrolysis oils can be used for other purposes, particularly as additives in refining or as feedstock for the production of valuable chemicals. Pyrolysis also requires milder temperatures than gasification, making the process less prone to the energy inefficiencies

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Abbreviations: CLSR, chemical looping steam reforming; HAc, acetic acid; T_{OX}, temperature of oxidation; T_{SR}, temperature of steam reforming; TGA-FTIR, thermogravimetric analysis coupled to Fourier transform infrared spectroscopy; TEM and SEM, transmission electron microscope and scanning electron microscope; X_{HAc} and X_{H2O}, conversion fraction of acetic acid and water respectively; $\dot{n}_{out,dry}$, total molar flow rate dry basis; n_i, number of moles of specie i; y_i and y_a, molar fraction of specie i and all gases in the outlet gas respectively; Sel_i, selectivity of individual constituent; W_i, molar weight of specie i; $\dot{n}_{i,in}$ and $\dot{n}_{i,out}$, molar flow rate in and out of specie I respectively; n_{Cgas}, number of moles of carbon gasified in air feed stage; $n_{Ni,t}$ and $n_{Ni(i)}$, number of moles of nickel oxidised and number of moles of nickel in catalyst; ($\dot{n}_{Ni\rightarrow NiO}$) and ($\dot{n}_{c,gas}$), rates of nickel oxidation of the reduced catalyst and rate of carbon gasified, respectively; $X_{Ni\rightarrow NiO}$, X_{C-gas}, extent of nickel and carbon oxidation; OC, oxygen carrier; sccm, standard cubic centimeters per minute; cc/g, cubic centimetre per gram; CHNS, carbon, hydrogen and nitrogen elemental analysis; BET, Brunauer–Emmett–Teller method; ICP-MS, inductively coupled plasma mass spectrometry; TOC, total organic carbon; S/C, steam to carbon ratio

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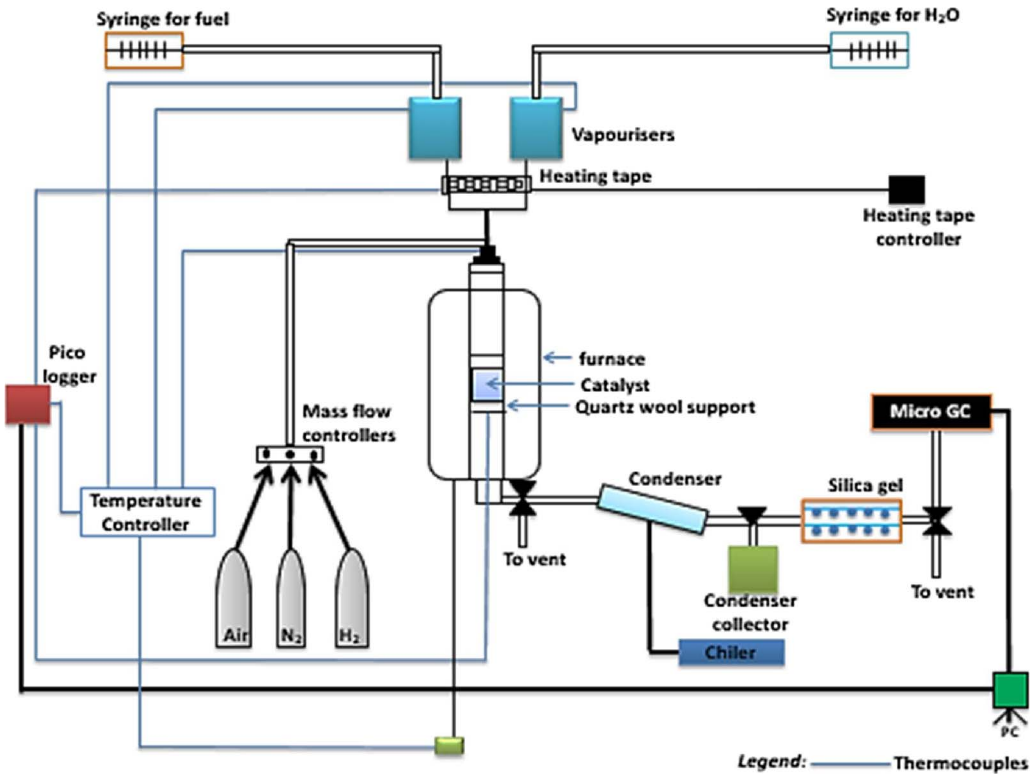

Fig. 1. Reactor set-up for evaluation of the CLSR-HAc cycles.

associated with the irreversibilities caused by large temperature gradients in the system. Finally, pyrolysis operates at lower pressure, thus safer, conditions. Bio-oils are chemically complex and rather unstable mixtures which has prompted the study on the utilisation of aqueous fractions of pyrolysis oils, model compounds or mixtures and oxygenates for pilot scale research and studies [8–15].

Acetic acid is one of the most studied model compound of pyrolysis oils for the production of hydrogen; this is due to its dominant presence in most bio-oil compositions [16,17]. Its thermal conversion to hydrogen, however, has been characterised with challenges due to side reactions and formation of intermediates particularly on the surface of the catalyst [9]. These have increased the need for process intensification and optimisation measures with the view of reducing some of the downsides encountered, as well as reducing the energy cost of the process.

The conventional process of steam reforming of acetic acid to hydrogen has been well researched [9,12,18–20]. Basagiannis and Verykios concluded that the reforming of acetic acid is complicated due to side reactions prominent at lower reforming temperatures, they also stipulated that the rate of carbon deposition observed on the catalyst is generally determined on the reforming temperature, catalyst utilised and the feed to steam ratio [21].

Process intensification measures particularly chemical looping steam reforming (CLSR) has been promoted to ease the challenges observed in the steam reforming process [22]; CLSR utilises an ‘oxygen transfer material’ (OTM) also known as ‘oxygen carrier’ (OC) which drives the reactions in a cyclic process as follows. As the steam reforming reactions are very endothermic, heat is provided at the heart of the process by the oxidation reactions in the reactor under air feed [23]. This ensures no dilution of the reformate mix product with diluent N_2 when the feed flow is switched to fuel feed and steam, some of fuel being sacrificed first to reduce the OC and thus activate it as a catalyst of the steam reforming and water gas shift reactions. The use of external burners to heat up the reformer and the costs associated with the use of highly corrosion resistant materials and combustion control techniques are thus avoided, while the absence of large temperature gradients during heat transfer reduces process irreversibilities and thus increases thermodynamic efficiency. The OC catalyst as utilised in this study should nevertheless have suitable characteristics particularly a high resistance to attrition, agglomeration and carbon deposition [24,25].

Previous reported works on the CLSR of acetic acid and other liquids of biomass origin have been centred on the reactivity of the catalyst across the looping cycles; it has been reported that the fuel conversion and consequently hydrogen yield reduces upon cycling for the CLSR of bio-diesel and scrap tyre pyrolysis oils [23,26]. Other studies indicated that no deterioration occurs in fuel conversion and hydrogen yield from the CLSR of other liquids of biomass origins investigated [27–29]. Thus, the efficiency of the fuel conversion and hydrogen yield of CLSR is influenced by the feedstock and operating conditions utilised, and the deterioration of the reactivity of the catalyst is generally due to carbon deposition, sintering and thermal decomposition of the feedstock.

This paper studies the redox cycling ability and process efficiency of chemical looping steam reforming of acetic acid (CLSR-HAc) in a packed bed reactor; ten experimental cycles were performed using the experimental approach as described in the next section. The auto-reduction activity of acetic acid of one of the nickel catalyst utilised in the present study has been previously investigated and it has been established that acetic acid performs considerably well when compared to the same catalyst after reduction by hydrogen [30]. The process outputs, hydrogen yield, conversion and selectivity to carbon gases for each cycle and two OC catalysts were compared with the view to measure consistency across the cycles; and characterisation of the catalysts was also done post-experimentally to ascertain any changes in morphology. The effect of the oxidation temperature on the reforming process was examined to ascertain its influence on the reforming process and full carbon balances were conducted to evaluate the share of solid carbon by-product during the process.