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# Hydrogen production from bio-oil: a thermodynamic analysis of sorption-enhanced chemical looping steam reforming

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## Abstract

The steam reforming of pyrolysis bio-oil is one proposed route to low carbon hydrogen production, which may be enhanced by combination with advanced steam reforming techniques. The advanced reforming of bio-oil is investigated via a thermodynamic analysis based on the minimisation of Gibbs Energy. Conventional steam reforming (C-SR) is assessed alongside Sorption Enhanced Steam Reforming (SE-SR), Chemical Looping Steam Reforming (CLSR) and Sorption Enhanced Chemical Looping Steam Reforming (SE-CLSR). The selected CO<sub>2</sub> sorbent is CaO(s) and oxygen transfer material (OTM) is Ni/NiO. PEFB bio-oil is modelled as a surrogate mixture and two common model compounds, acetic acid and furfural, are also considered. A process comparison highlights the advantages of sorption-enhancement and chemical looping, including improved purity and yield, and reductions in carbon deposition and process net energy balance.

The operating regime of SE-CLSR is evaluated in order to assess the impact of S/C ratio, NiO/C ratio, CaO/C ratio and temperature. Autothermal operation can be achieved for S/C ratios between 1 and 3. In autothermal operation at 30 bar, S/C ratio of 2 gives a yield of 11.8wt%, and hydrogen purity of 96.9mol%. Alternatively, if autothermal operation is not a priority, the yield can be improved by reducing the quantity of OTM. The thermodynamic analysis highlights the role of advanced reforming techniques in enhancing the potential of bio-oil as a source of hydrogen.

## Keywords

Bio-oil; Steam reforming; Chemical looping; Sorption enhancement; Thermodynamic analysis

## 1. Introduction

Hydrogen is an important chemical feedstock for various applications, including the chemicals sector, crude oil refining and fertiliser manufacture [1]. There is also interest in hydrogen as a clean energy vector for a range of applications, including transport, heating and energy storage [2,3]. As the energy system is undergoing considerable transition, the nature of the future energy mix remains unclear, but it is evident that hydrogen use can be expected to grow in a number of sectors [4,5].

Most hydrogen is produced by the steam reforming of fossil fuels [6]. The steam reforming reaction releases hydrogen from the fuel, but also releases carbon in the form of CO<sub>2</sub>. Further CO<sub>2</sub> is released from fuel combustion, which is required to heat the endothermic reaction. As a result, steam methane

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reforming releases around 10 to 12 kg CO<sub>2</sub> for each kg of H<sub>2</sub> produced [7,8]. Annual global emissions from hydrogen production are around 500 megatonnes CO<sub>2</sub> per year [5], which was equivalent to approximately 1.4% of the total CO<sub>2</sub> emissions from fossil fuels and industry in 2016 [9]. To continue to meet hydrogen demand within a decarbonised economy, it is necessary to establish low carbon methods of hydrogen production on a large scale.

While life cycle assessment has shown that fossil fuel steam reforming has a high carbon footprint compared to other hydrogen production methods, the process is capable of producing hydrogen cost-effectively and efficiently at large scale [10]. If steam reforming could be combined with methods to reduce emissions, such as low carbon feedstocks and Carbon Capture Utilisation and Storage (CCUS), it may be a promising solution for efficient, large scale production of low carbon hydrogen.

One means of reducing the carbon emissions, as well as reducing dependence on fossil fuels, is to use a feedstock derived from bioenergy. There are multiple methods to convert the hydrogen-containing compounds within biomass to hydrogen. One method uses pyrolysis to convert solid biomass into bio-oil, which is subsequently used in a steam reforming process. Bio-oil is an energy-dense liquid containing a complex mixture of oxygenated organic compounds. It can be transported as a liquid fuel, potentially enabling a network of decentralised pyrolysis plants which serve a central steam reforming facility [1]. Bio-oil steam reforming can reduce greenhouse gas emissions by around 50% compared to natural gas, depending on the source of the biomass [11].

Experimental studies of bio-oil steam reforming have demonstrated bio-oil conversions of over 90%, but highlighted that carbon deposition is a challenge for this chemically complex feedstock [12]. The risk of carbon deposition may be partly alleviated by catalyst selection. Low cost nickel-based catalysts are capable of breaking the C-C bonds in the bio-oil, and have high activity for steam reforming, but they are also very active for coke formation and methanation. Noble metals have demonstrated higher reforming activities and reduced carbon deposition, but the cost can be prohibitive. Another approach includes modifying Ni-based catalysts with promoters, including metals such as Cu, Co and Zn, or metal oxides such as La<sub>2</sub>O<sub>3</sub>, MgO and CaO [13,14].

Steam reforming may also be improved using advanced process techniques, such as sorption enhancement and chemical looping. In Sorption-Enhanced Steam Reforming (SE-SR), the reaction is enhanced by the addition of a solid CO<sub>2</sub> sorbent [15]. The sorbent removes CO<sub>2</sub> from the reactor, enhancing purity and enabling in situ CO<sub>2</sub> capture. At the same time, it shifts the chemical equilibrium, thereby improving hydrogen yield. A range of sorbents have been studied, including MgO, hydrotalcite, Li<sub>2</sub>O<sub>3</sub> and alkaline ceramics. CaO has been identified as a promising sorbent with high capacity and low cost, although long-term stability remains a challenge [16,17].

In chemical looping steam reforming (CLSR), an oxygen transfer material (OTM) provides an undiluted source of oxygen for partial oxidation of the fuel, thereby enabling an autothermal reforming process without costly air separation [18]. It is closely related to other chemical looping processes proposed for hydrogen production, such as steam reforming with chemical looping combustion (SR-CLC), or chemical looping water splitting [19–23].

Early studies such as those by Fathi et al. [24] and Rydén et al. [25] demonstrated the feasibility of CLSR. Over 700 OTMs have since been developed and tested for combustion and reforming [19], aiming to produce materials with high catalytic activity and stability [26–29]. OTMs are typically comprised of a metal oxide such as Cu, Fe<sub>2</sub>O<sub>3</sub>, NiO, or Mn<sub>3</sub>O<sub>4</sub> supported on an inert material such as Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub>, TiO<sub>2</sub> or ZrO<sub>2</sub> [30]. Nickel-based OTMs are the most extensively analysed in literature [19] and have the crucial advantage in packed bed configuration of being the best steam reforming catalysts in their reduced, metallic form. Studies with methane and Ni/NiO have demonstrated high reactivity and stability at high temperatures, as well as high selectivity towards hydrogen production [28,30–32]. The CLSR concept has also been applied to alternative fuels from bioenergy sources, including glycerol [33,34], waste lubricating oil [35], and bioethanol [36]. This also includes the CLSR of bio-oil and its model compounds on nickel-based OTMs [37–39].

The advantages of sorption enhancement and chemical looping can be combined into SE-CLSR, to give high purity hydrogen in an autothermal process [32,40–42]. Recent work has demonstrated the performance of acetic acid in SE-CLSR, as a model compound for bio-oil [43]. Over 20 successive cycles at 923K, the yield remained above 78% of the equilibrium value.

These results suggest that there is an opportunity to combine advanced reforming techniques with bio-based feedstocks. The advantages of advanced reforming techniques, such as improved yields, efficiencies and flexibility of scale, could strengthen the technical and economic case for the uptake of alternative feedstocks. At the same time, there are advantages to developing the next generation of steam reforming techniques in parallel with an understanding of future fuels. In particular, enabling cost-effective carbon capture in bio-oil steam reforming would unlock a new type of bioenergy with carbon capture and storage (BECCS), which has been identified as a vitally important source of negative emissions [44].

In this study, a thermodynamic analysis is carried out to evaluate hydrogen production from bio-oil. Thermodynamic analysis is an informative tool which can be used to evaluate key process parameters such as equilibrium yields, conversions and the energy balance. It is a first step towards more realistic, dynamic models, capable of simulating real processes and demonstrating real improvements over conventional steam reforming of fossil fuels. This technique has been used to investigate advanced reforming of several feedstocks, including methane [42,45], shale gas [41] and glycerol [46]. Thermodynamic analysis has also been carried out on bio-oil model compounds in conventional steam reforming, SE-SR and CLSR [47–50].

Two opportunities have been identified to improve understanding of the advanced reforming of bio-oil. First is the study of SE-CLSR, which has not previously been examined for bio-oil. Second is the modelling of bio-oil as a mixture of compounds, rather than a single model compound, to give a closer assessment of its potential. This work examines three feedstocks relating to bio-oil: a bio-oil surrogate mixture, and two model compounds. The steam reforming techniques studied include conventional steam reforming (C-SR), sorption-enhanced steam reforming (SE-SR), chemical looping steam reforming (CLSR), and sorption-enhanced chemical looping steam reforming (SE-CLSR).

Thermodynamic analysis is applied to evaluate an approximate energy balance of bio-oil reforming processes, as well as the hydrogen yield, product purity, and potential for carbon deposition. The autothermal operation of SE-CLSR is assessed, to identify opportunities for optimisation. Given the high oxygen content of bio-oils and lower calorific value, important questions addressed in this study are whether sufficient heat can be generated by the unmixed oxidation of the bio-oil surrogate mixture and the two model compounds to supply the demand of their steam reforming, and whether the requirement for sorbent material does not overwhelm the heat balance due to larger CO<sub>2</sub> generation, both necessary to maintain cyclic operation.

## 2. Process description

In conventional steam reforming (C-SR), a hydrocarbon or other organic fuel reacts with steam to produce hydrogen and carbon dioxide (R1 to R3 in Table 1). In industry, the reaction typically occurs in two reactor stages: a reforming stage and a water gas shift (WGS) stage. The reforming reactor performs the endothermic R1 at high temperature, producing syngas. The WGS reactor reduces the carbon monoxide content via the exothermic R2, increasing H<sub>2</sub> yield and purity [51]. This study focusses on the high temperature reforming stage.

Three advanced reforming processes are also considered: SE-SR, CLSR and SE-CLSR. In SE-SR, a CO<sub>2</sub> sorbent is added to the reforming reactor. The sorption of CO<sub>2</sub> shifts the chemical equilibrium and provides heat, resulting in improved yield and purity, as well as achieving in situ capture of CO<sub>2</sub> [15]. In CLSR, an oxygen transfer material (OTM), typically a metal oxide, provides oxygen for partial oxidation of the fuel (R9). In its reduced form, the OTM acts as a catalyst for the reforming reaction, so that fuel oxidation in the absence of air occurs simultaneously with reforming. The release of heat from fuel oxidation reduces energy demand, so that the reformer may be autothermal, and no longer requires indirect heating from a furnace. The OTM provides oxygen in an undiluted form, thereby eliminating the need for costly air separation [18]. SE-CLSR combines sorption enhancement with the chemical looping principle, bringing about added benefits through combination of equilibrium shift, steam reforming and OTM reduction.

To enable regeneration of sorbent and re-oxidation of the OTM, these advanced reforming processes are cyclical. The cycle steps can occur in a series of fluidised beds, or within a packed bed with sequenced flows [30,52]. The cycles of SE-SR, CLSR and SE-CLSR in a packed bed have previously been illustrated in S G Adiya et al [41].

In these processes, steam reforming occurs alongside reactions of the OTM and sorbent. In addition, a number of reactions lead to coke formation [53]. Table 1 shows the generalised reaction scheme for an organic compound C<sub>n</sub>H<sub>m</sub>O<sub>k</sub>. On the basis of the literature review, the selected OTM is Ni/NiO. The selected CO<sub>2</sub> sorbent is CaO<sub>(s)</sub>.

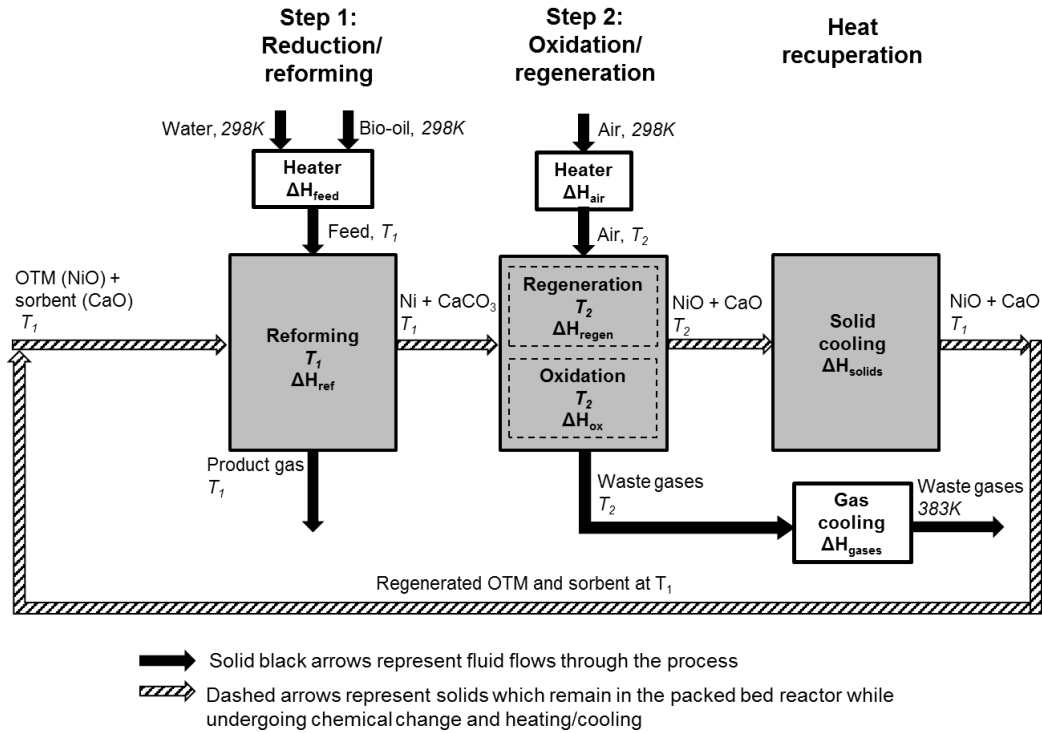
**Table 1 - Main reactions in sorption-enhanced and chemical looping reforming of an organic compound  $C_nH_mO_k$** 

No.	Reaction	Description
R1	$C_nH_mO_k + (1 - k)H_2O \leftrightarrow CO + \left(\frac{m}{2} - k + 1\right)H_2$	Steam reforming
R2	$CO + H_2O \leftrightarrow CO_2 + H_2$	Water gas shift
R3	$C_nH_mO_k + (2n - k)H_2O \leftrightarrow nCO_2 + \left(2n + \frac{m}{2} - k\right)H_2$	Global steam reforming
R4	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	Methanation
R5	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	Methanation
R6	$CaO_{(s)} + CO_2 \leftrightarrow CaCO_{3(s)}$	Carbonation of $CaO_{(s)}$
R7	$CaO_{(s)} + H_2O \leftrightarrow Ca(OH)_{2(s)}$	Hydration of $CaO_{(s)}$
R8	$C_nH_mO_k + (2n - k)H_2O + nCaO \rightarrow nCaCO_3 + \left(2n + \frac{m}{2} - k\right)H_2$	Sorption-enhanced steam reforming
R9	$C_nH_mO_k + \left(\frac{3n}{2} - k\right)NiO \rightarrow \left(\frac{3n}{2} - k\right)Ni + \frac{n}{2}CO + \frac{n}{2}CO_2 + \frac{m}{2}H_2$	Reduction of NiO/oxidation of fuel
R10	$C_nH_mO_k + \left(n - \frac{2k}{3}\right)NiO + \left(n - \frac{k}{3}\right)H_2O$ $\rightarrow \left(n - \frac{2k}{3}\right)Ni + nCO_2 + \left(n + \frac{m}{2} - \frac{k}{3}\right)H_2$	CLSR (combined NiO reduction and global steam reforming).
R11	$C_nH_mO_k + \left(n - \frac{2k}{3}\right)NiO + \left(n - \frac{k}{3}\right)H_2O + nCaO$ $\rightarrow \left(n - \frac{2k}{3}\right)Ni + nCaCO_3 + \left(n + \frac{m}{2} - \frac{k}{3}\right)H_2$	SE-CLSR (combined NiO reduction and sorption-enhanced steam reforming)
R12	$Ni_{(s)} + 0.5O_2 \rightarrow NiO_{(s)}$	Oxidation of Ni
R13	$C_nH_mO_k \leftrightarrow C_xH_yO_z + gases (H_2, H_2O, CO, CO_2, CH_4 \dots) + coke$	Thermal pyrolysis reaction
R14	$2CO \leftrightarrow CO_2 + C$	Boudouard reaction
R15	$CO + H_2 \leftrightarrow C + H_2O$	Coke formation from CO
R16	$CH_4 \leftrightarrow C + 2H_2$	Coke formation from $CH_4$

### 3. Methodology

#### 3.1. Energy balance

Fig. 1 illustrates the main components in the energy balance for the SE-CLSR process. As well as the heat associated with reactions, the balance also includes heating of reactants, and heat recuperation from the solids and waste gases.



**Fig. 1. Schematic description of SE-CLSR, showing key energy terms and temperature assumptions.**

The  $\Delta H$  terms were based on the definitions given in [41]. In this study, they are defined as:

$\Delta H_{\text{feed}}$  is the enthalpy change required to raise liquid reactants from 298K to reforming temperature ( $T_1$ ).

$\Delta H_{\text{ref}}$  is the enthalpy associated with the reactions in the reduction/reforming step, occurring isothermally at  $T_1$ .

$\Delta H_{\text{regen}}$  is the enthalpy associated with sorbent regeneration, including the heating of the sorbent from  $T_1$  to  $T_2$ , and the enthalpy of reaction. For a 1.013 bar system, the regeneration temperature was set at 1170K. For higher pressure systems, the temperature was raised to ensure full regeneration of the sorbent.  $T_2$  is 1240K, 1300K and 1420K for a 5 bar, 10 bar and 30 bar system respectively.

$\Delta H_{\text{air}}$  is the enthalpy change required to heat air from 298K to regeneration/oxidation temperature ( $T_2$ ).

$\Delta H_{\text{ox}}$  is the enthalpy released by oxidation of Ni, at  $T_2$ . Where there is solid carbon present in the equilibrium products,  $\Delta H_{\text{ox}}$  also includes the oxidation of this carbon.

$\Delta H_{\text{solids}}$  is the enthalpy change associated with heating or cooling the regenerated solids (NiO and CaO) from  $T_2$  to reformer temperature ( $T_1$ ), so that they are returned to the starting point of the next cycle.

$\Delta H_{\text{gases}}$  is the heat recuperated from cooling the waste gases from step 2. This includes unreacted  $N_2$  from the air, and the  $CO_2$  released by sorbent regeneration. Gases are cooled from  $T_2$  to 383K.

$\Delta H_{\text{total}}$  is the overall energy balance, calculated as the sum of all the energy terms.

For C-SR:  $\Delta H_{total} = \Delta H_{feed} + \Delta H_{ref}$

For SE-SR:  $\Delta H_{total} = \Delta H_{feed} + \Delta H_{ref} + \Delta H_{regen} + \Delta H_{solids} + \Delta H_{gases}$

For CLSR:  $\Delta H_{total} = \Delta H_{feed} + \Delta H_{ref} + \Delta H_{air} + \Delta H_{ox} + \Delta H_{solids} + \Delta H_{gases}$

For SE-CLSR:  $\Delta H_{total} = \Delta H_{feed} + \Delta H_{ref} + \Delta H_{air} + \Delta H_{ox} + \Delta H_{regen} + \Delta H_{solids} + \Delta H_{gases}$

Where a unit was exothermic, this was signified by a negative energy term. Where  $\Delta H_{total}$  was equal to or less than zero, the process as a whole is autothermal.

An Aspen Plus simulation was used to calculate the terms in the energy balance. Reactors were modelled using RGibbs reactor blocks, which calculate thermodynamic equilibrium by the minimisation of Gibbs free energy. The selected property method was Peng-Robinson [54]. A series of two reactors, with the solids flowing from one reactor to another, was used to represent the two main cycle stages. In C-SR, SE-SR and CLSR, the absence of OTM or sorbent was modelled by setting the flow of the corresponding stream to zero.

To assess the potential for carbon deposition, solid carbon (graphite) was included as a component within Aspen Plus. Fluid inputs (fuel, water, air) enter the system at 298K, and at operating pressure. The energy balance did not include the energy required to raise the fluids to this pressure, or any other electrical or auxiliary energy. The flow of air was set by a calculator block, which calculated the stoichiometric quantity of air required to completely oxidise the nickel. The composition of air was assumed as 79% N<sub>2</sub> and 21% O<sub>2</sub>.

Key process parameters are the steam-to-carbon (S/C) ratio, NiO to carbon (NiO/C) ratio and sorbent to carbon (CaO/C) ratio. The flow of steam, Ni and CaO were set using a calculator block, which multiplied the molar carbon flow by the relevant ratio. For S/C ratio, the calculation took account for the water content in the bio-oil:

$$n_{steam} = \left( \sum \alpha_i n_{C,bio-oil} \times S \right) - y_{H_2O} n_{bio-oil}$$

Where  $n_{steam}$  and  $n_{bio-oil}$  are the molar flow rates of steam and bio-oil respectively. S is the S/C ratio,  $y_{H_2O}$  is the molar fraction of water in bio-oil,  $n_{C,bio-oil}$  represents the number of moles of carbon species in the bio-oil, and  $\alpha_i$  is the number of carbon atoms in the carbon species.

The yield was expressed as wt% of the feedstock. As the bio-oil has a high moisture content (Table 2), the yield was expressed on a wet basis and moisture-free (m.f.) basis:

$$H_2 \text{ yield (wt\%, wet)} = \frac{n_{H_2} \times MW_{H_2}}{n_{fuel,wet} \times MW_{wet}} \times 100$$

$$H_2 \text{ yield (wt\%, m. f. )} = \frac{n_{H_2} \times MW_{H_2}}{n_{fuel,m.f.} \times MW_{m.f.}} \times 100$$



Where  $n_{H_2}$  is the number of moles of hydrogen produced, and  $MW_{H_2}$  is the molecular weight of hydrogen.  $n_{fuel,wet}$  represents the number of moles of fuel including moisture content, and  $MW_{wet}$  is its molecular mass.  $n_{fuel,m.f.}$  is the number of moles of the organic fraction of the fuel, and  $MW_{m.f.}$  is its molecular mass.

The yield was also expressed as a percentage of the theoretical potential from the SE-CLSR global reaction (R11):

$$H_2 \text{ yield (\% of stoich. potential)} = \frac{\text{mol } H_2 \text{ produced}}{\text{mol } H_2 \text{ from SE-CLSR stoichiometry}} \times 100$$

Purity was calculated as the molar percentage of hydrogen in the product gas, on a dry basis:

$$H_2 \text{ purity (mol \%)} = \frac{n_{H_2,product}}{n_{total,product} - n_{H_2O,product}} \times 100$$

Where  $n_{i,product}$  is the number of moles of component i in the product gas.

### 3.2. Feedstocks

Three different feedstocks were considered: acetic acid, furfural, and bio-oil surrogate mixture. Bio-oil has a complex chemical composition, which varies between different feedstocks and processes [55], so that studies commonly used a single model compound as an approximation. Acetic acid is often used, as it is one of the most abundant compounds found in compositional analysis [12,56–58]. In this study, furfural was also selected because its molecular formula ( $C_5H_4O_2$ ) closely matches that of the moisture-free bio-oil model mixture shown in Table 3. Furfural has been used as a model compound by several authors [38,59]. Remón et al [60] used a statistical analysis to identify that acetic acid and furfural were the compounds which had the most significant effect on bio-oil reforming performance.

Bio-oil may also be simulated by a mixture of components, using a variety of approaches. Plou et al. [61] used mixtures of acetic acid, methanol and acetol to represent three major groups in bio-oil (acids, alcohols and ketones). Other authors have matched their mixture composition to a detailed compositional analysis, using around 10 different compounds [62,63]. An alternative approach involves using a selection of model compounds, in combinations that give an elemental composition ( $C_nH_mO_k$ ) matching that of a real bio-oil [64,65].

In this study, the composition of the bio-oil surrogate mixture was based on the work of Dupont et al. [66]. The bio-oil is represented as a mixture of the 6 macro-families identified by Garcia-Perez et al. [67]. The mass fraction of each compound was selected using curve fitting procedures, in order that the elemental composition and differential thermogravimetric (DTG) curve closely matches that of a real Palm Empty Fruit Bunch (PEFB) bio-oil [68]. A sensitivity analysis on PEFB bio-oil model mixtures has previously shown that the equilibrium results are not sensitive to the exact mixture composition, provided that the elemental composition is known [69]. The composition used in this study is shown in Table 2.

**Table 2 – PEFB bio-oil model mixture composition[66,70]**

	C	H	O
Ultimate analysis, mol fraction <sup>a</sup>	0.286	0.491	0.223
Model mixture, mol fraction	0.268	0.519	0.213
Percentage of error, %	6.2	5.8	4.8
Water, wt.% <sup>a</sup>	24.3		
Model water, wt.%	24.0		
Family <sup>b</sup>	Family wt.%	Model compounds	Mass fraction
1	F1=10%	Formaldehyde, CH <sub>2</sub> O	0.08
		Acetaldehyde, C <sub>2</sub> H <sub>4</sub> O	0.01
		1-hydroxy-2-butanone, C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	0.01
2	F2=30%	Acetic acid, C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	0.07
		Water, H <sub>2</sub> O	0.23
3	F3=15%	Furfural, C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	0.13
		Phenol, C <sub>6</sub> H <sub>6</sub> O	0.01
		Water, H <sub>2</sub> O	0.01
4	F4=15%	Creosol, C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	0.14
		Guaiacol, C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	0.01
5	F5+F6=30%	Catechol, C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	0.24
6		Palmitic acid, C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	0.01
		Levoglucosan, C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	0.05

<sup>a</sup> Composition of real PEFB bio-oil is from Pimenidou and Dupont [68]

<sup>b</sup> Macro-families are based on Garcia-Perez[67]

Table 3 shows the key stoichiometric information for each feedstock in SE-CLSR (R11). Methane is also included for comparison, as it is a common steam reforming feedstock. The stoichiometry illustrates some key constraints, such as the potential hydrogen yield, required S/C ratio and appropriate quantities of OTM and sorbent.

**Table 3 - Summary of stoichiometry for SE-CLSR of methane, bio-oil model compounds, and PEFB bio-oil surrogate mixture (Reaction 11)**

		Methane	Acetic acid	Furfural	PEFB bio-oil (moisture-free)
Composition (C <sub>n</sub> H <sub>m</sub> O <sub>k</sub> )	n	1	2	5	4.057
	m	4	4	4	4.977
	k	0	2	2	1.776
Molar mass (kg/kmol)		16.05	60.06	96.09	82.17
Reactants (mol <sub>i</sub> mol <sub>feedstock</sub> <sup>-1</sup> )	NiO	1.000	0.667	3.667	2.873
	H <sub>2</sub> O	1.000	1.333	4.333	3.465
	CaO	1.000	2.000	5.000	4.057
Products (mol <sub>i</sub> mol <sub>feedstock</sub> <sup>-1</sup> )	Ni	1.000	0.667	3.667	2.873
	CaCO <sub>3</sub>	1.000	2.000	5.000	4.057
	H <sub>2</sub>	3.000	3.333	6.333	5.954
S/C ratio		1.000	0.667	0.867	0.854
NiO/C ratio		1.000	0.333	0.733	0.708
CaO/C ratio		1.000	1.000	1.000	1.000
mol <sub>H<sub>2</sub></sub> mol <sub>carbon</sub> <sup>-1</sup>		3.000	1.667	1.267	1.468

## 4. Results and discussion

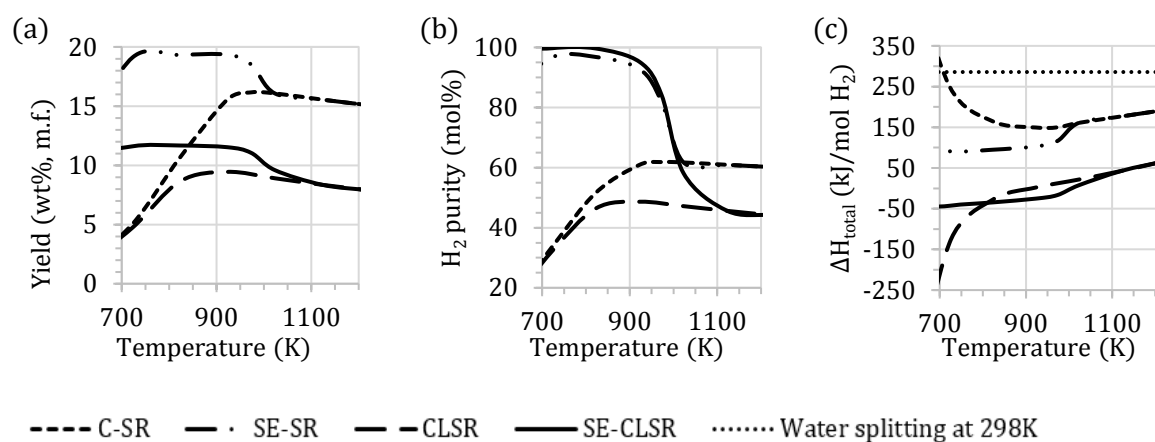
### 4.1. Process comparison and effect of temperature

Fig. 2 shows the performance of each process over a range of temperatures and at atmospheric pressure. Fig. 2a and Fig. 2b indicate that the sorbent enhances the yield and purity of C-SR and CLSR, until the sorbent becomes ineffective at around 1050K. At certain temperatures, the sorption

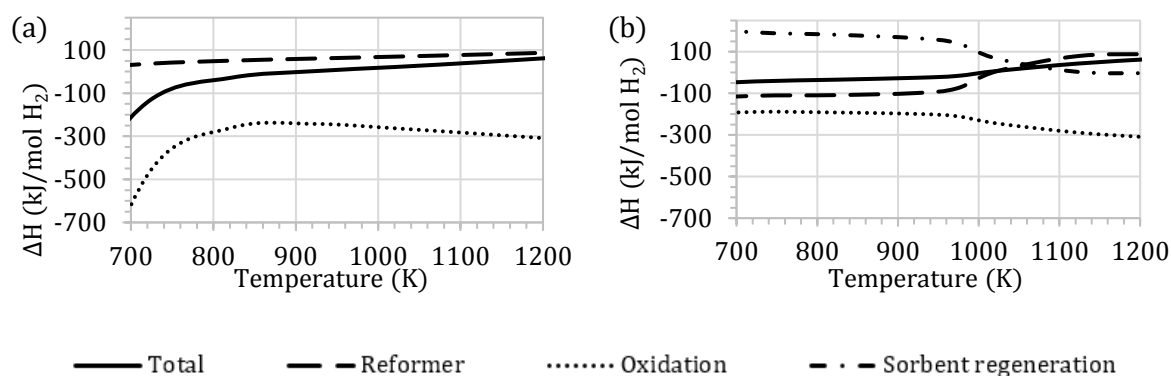
enhanced processes achieve purity over 99mol%, while C-SR and CLSR only reach 60mol% purity, and would require extensive downstream processing.

In SE-CLSR with S/C ratio of 2, maximum H<sub>2</sub> yield (11.7 wt%) is achieved at 823K, at which point the purity is 99.6mol% H<sub>2</sub>, with 0.2 mol% CO<sub>2</sub>, 0.1 mol% CH<sub>4</sub> and 0.05 mol% CO. However, maximum purity (99.7 mol%) is achieved at 723K, where yield is slightly lower than the maximum (11.6 wt%). The remaining 0.3% is methane, and other impurities are negligible (<1ppm). To reduce the requirement for downstream processing, the optimal operating point is likely to be the point of maximal purity, where yield will be slightly lower than the maximum.

As result of the enhanced yield, SE-SR has a lower net energy balance than C-SR, despite the requirement for heat to regenerate the sorbent (Fig. 2c). At atmospheric pressure, SE-CLSR has a lower net energy balance than CLSR only between the range of around 800 – 1050 K. This can be explained by the individual energy terms, shown in Fig. 3. Below 800K, the CLSR energy balance is dominated by the oxidation term. Both CLSR and SE-CLSR release the same quantity of heat in oxidation but CLSR has a very low yield in this region, so that the energy released per mole of H<sub>2</sub> is higher. While CLSR appears to have a thermodynamic advantage over SE-CLSR at this point, it is unlikely that the process would be operated in this region as the yield is low. Above 1050K, the calcium sorbent becomes ineffective and so both CLSR and SE-CLSR have the same net energy balance. The design of advanced reforming processes should consider these interactions between yield and heating burden in order to find an optimal balance.



**Fig. 2** - The effect of reduction/reforming temperature ( $T_1$ ) for PEFB bio-oil surrogate mixture in C-SR, CLSR, SE-SR and SE-CLSR with S/C ratio of 2 at 1.013 bar. For SE-SR and SE-CLSR, CaO/C = 1 and NiO/C = 1. (a) mass yield, moisture-free basis, (b) H<sub>2</sub> purity, (c) net process energy balance.



**Fig. 3** - The effect of reduction/reforming temperature ( $T_1$ ) on the main energy terms in advanced reforming of PEFB bio-oil surrogate mixture with  $S/C = 2$  at 1.013 bar (a) CLSR, with  $NiO/C = 1$  and  $CaO/C = 0$ , (b) SE-CLSR, with  $NiO/C = 1$  and  $CaO/C = 1$ .

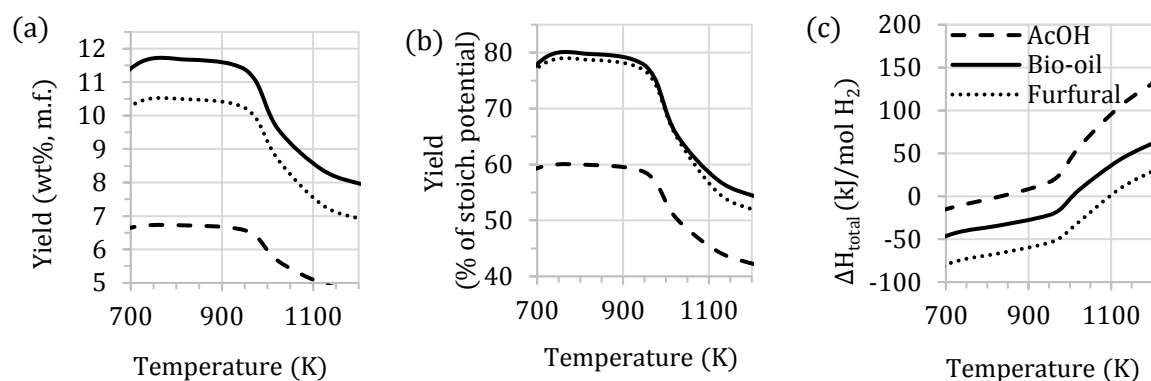
The equilibrium yields for the PEFB bio-oil mixture are similar to yields observed in experimental studies. Remón et al. [60] measured steam reforming yields in the range of 10 to 18 wt% from various bio-oils at  $S/C = 7.6$  and 923K. At the same conditions, the C-SR equilibrium model gives 11.6 wt% m.f. For a real PEFB bio-oil, Zin et al. [71] measured a yield of 9.5 wt% m.f. with  $S/C = 2.75$  at 873K. Sorption enhancement increased the yield to 10.4 wt%, with  $H_2$  purity of 97%. At the same conditions, the model gives 16.2 wt% m.f and 21.1 wt% m.f. in SR and SE-SR respectively. A direct comparison is not applicable as the molecular composition was different in each case. Nonetheless, these figures indicate that the surrogate mixture gives predictions within a reasonable range.

Experimental demonstration of advanced reforming of bio-oil is more limited, but there is some evidence of model compounds achieving close to equilibrium yield in CLSR. In CLSR at 923K, acetic acid achieved 7.13 wt%, or 61.27% of equilibrium yield, while furfural achieved 12.6 wt%, or 71.86% of equilibrium yield [47].

One limitation of thermodynamic analysis is that it does not represent the deactivation of OTM and sorbent over multiple cycles. Acetic acid has displayed stable performance over at least 10 successive cycles in CLSR and SE-CLSR, with carbon deposits being removed during the oxidation stage [39,43]. However, a whole bio-oil may display different deactivation behaviour. Catalyst stability is not within the scope of this study, but it is an important consideration for future work on process feasibility.

#### 4.2. Feedstock comparison in the SE-CLSR process

The previous section focussed on bio-oil surrogate mixture, but it is also useful to understand how common model compounds perform in the same analysis. Fig. 4 shows the yield and net energy balance for each feedstock in SE-CLSR.



**Fig. 4** - The effect of reduction/reforming temperature ( $T_1$ ) in SE-CLSR of acetic acid, bio-oil and furfural at 1.013 bar with  $S/C = 2$ ,  $NiO/C = 1$ ,  $CaO/C = 1$  (a) mass yield, moisture-free basis, (b) yield in % of stoichiometric potential from the SE-CLSR global reaction, (c) yield in mol  $H_2$  product per mol of  $H_2$  in feedstock, (d) net process energy balance

Fig. 4a shows the mass yield, as this parameter is commonly used for reporting experimental results in bio-oil reforming. The mass yield from bio-oil peaks at 11.7 wt% m.f., while acetic acid achieves only 6.7 wt% m.f. This is explained by the stoichiometry in Table 3. Although bio-oil has a higher molar mass (i.e. a higher denominator), this is balanced by a high molar yield. When the stoichiometric yield is used (Fig. 4b), bio-oil and furfural are closely matched due to the similarity in their chemical formula shown in Table 3 ( $C_nH_mO_k$ ). The behaviour of furfural more closely models that of the bio-oil, suggesting that it is a more suitable model compound for representing the performance of bio-oil.

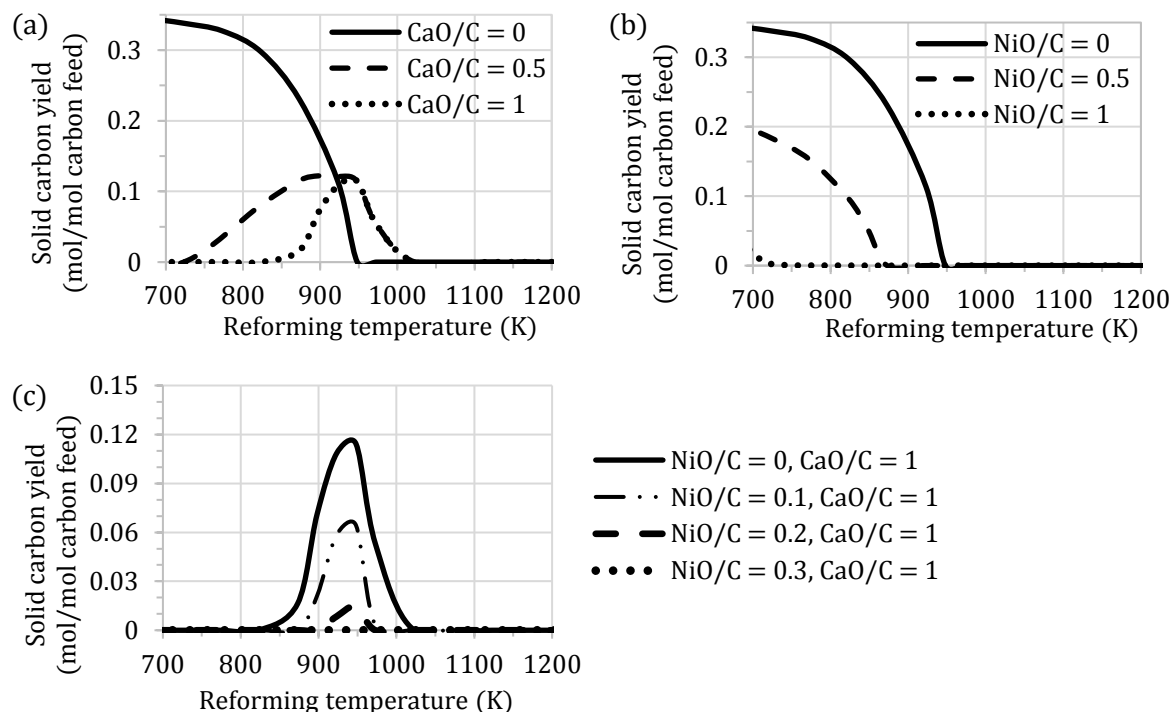
Figure 4c shows the wide variation in net energy balance between the different feedstocks. At the range of conditions considered, the furfural energy balance is lower than that of bio-oil, by 32 to 37 kJ mol $H_2^{-1}$ . The net energy balance for acetic acid is higher than that of bio-oil, by 30 to 72 kJ mol $H_2^{-1}$ . In the optimal region, both model compounds are a similar distance from the bio-oil mixture. This highlights that variations in bio-oil composition could have a large impact on the energy balance, so that feedstock variation would be an important factor in process design and control.

These results were generated using the same  $NiO/C$  ratio ( $NiO/C = 1$ ). In practice, each feedstock will have a different optimal  $NiO/C$  ratio, according to the reaction stoichiometry (Table 3). For example, acetic acid appears to be performing well beneath its stoichiometric potential in Figure 4b, but this is because  $NiO/C$  of 1 represents a large excess of  $NiO$  above the required level (0.333). Thus, it is not appropriate to make a direct comparison of feedstocks at a single set of conditions. Instead, the process should be optimised, and the different optimal solutions compared. Section 4.4 examines this optimisation.

#### 4.3. Carbon deposition

At  $S/C$  ratio of 2 and above, the results showed no carbon deposition in bio-oil steam reforming. A high excess of steam inhibits carbon deposition, and enables steam gasification of any existing

carbon deposits [41]. However, operating with a lower S/C may be preferable as it reduces the process energy balance. Section 4.4 contains further detail on the influence of S/C ratio on yield and energy balance. To understand the risk of carbon deposition at low S/C ratios, Fig. 5 shows solid carbon yields with S/C = 1.



**Fig. 5** - Equilibrium carbon product in the advanced reforming of PEFB bio-oil surrogate mixture with S/C = 1 at 1.013 bar (a) SE-SR, with NiO/C = 0, (b) CLSR, with CaO/C = 0, (c) SE-CLSR, with CaO/C = 1.

In SE-SR, the presence of sorbent changes the limit for carbon deposition (Fig. 5a). The upper temperature limit is increased, but a minimum temperature is also introduced, to give an envelope in which equilibrium carbon product occurs. As more sorbent is introduced, the lower limit increases so that the envelope for carbon deposition is narrowed. In SE-SR with a stoichiometric quantity of sorbent (CaO/C = 1), carbon deposition occurs between 823K and 973K. Previous thermodynamic studies have similarly found that carbon deposition is suppressed by CO<sub>2</sub> sorption. These studies suggest that the enhanced WGS reaction reduces CO content, and thus shifts the equilibrium for the Boudouard reaction (R14) backwards [72,73].

Figure 5b shows the effect of OTM content in CLSR. Increasing the amount of NiO moves the temperature boundary for carbon, so that carbon is eliminated at lower temperatures. By increasing NiO/C to 1, carbon product is eliminated at any temperature over 725K. This is the result of introducing oxygen into the reactor, which enables the oxidation of carbon.

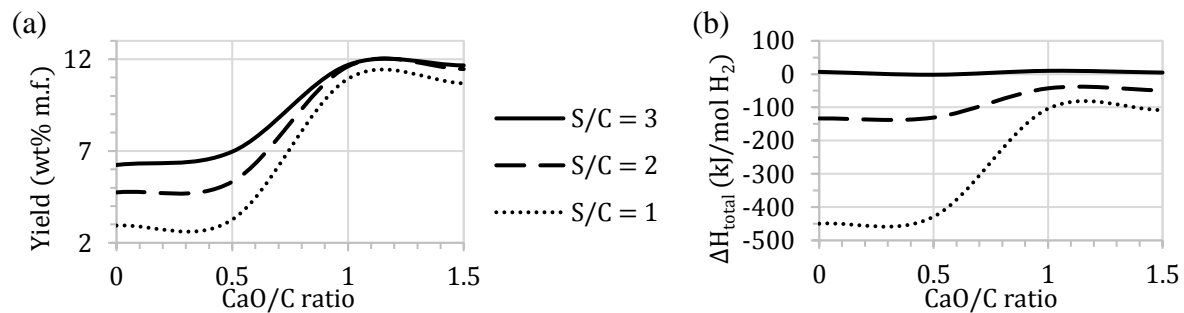
The combined effects of both OTM and sorbent in SE-CLSR are shown in Figure 5c. With CaO/C = 1, and S/C = 1, carbon product is eliminated with NiO/C of 0.3 or above. These results highlight a potential advantage of SE-CLSR: by combining the effects of the sorbent and OTM, carbon can be suppressed to very low levels across a wide operating range.

#### 4.4. Optimisation and autothermal operation in SE-CLSR of bio-oil

The analysis has highlighted that the process is affected by several interacting parameters which should be considered together. As well as temperature and pressure, other key parameters for consideration are the ratios S/C, NiO/C and CaO/C. These parameters can be manipulated to enhance yield and purity, reduce energy demand and eliminate carbon deposition.

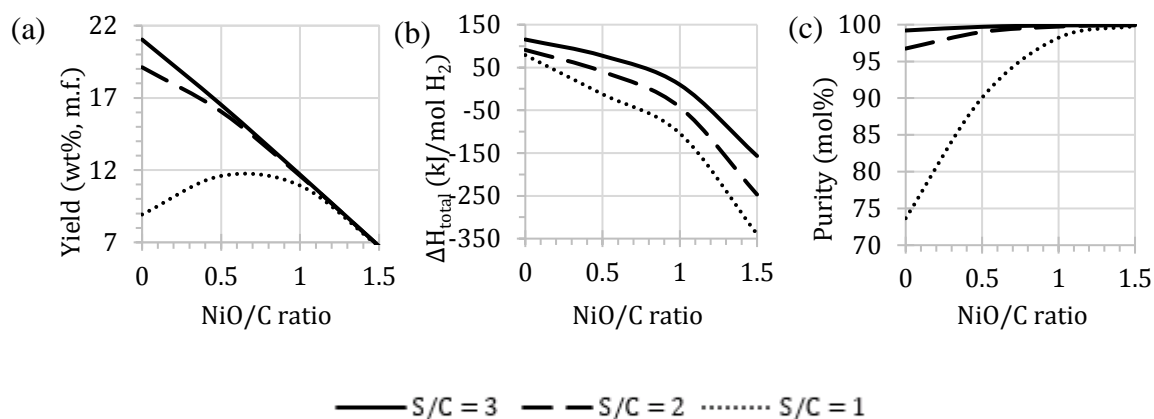
In this optimisation study of H<sub>2</sub> production from bio-oil, three parameters are initially fixed: pressure, temperature, and CaO/C ratio. According to Le Chatelier's principle, the reaction is favoured by low pressures, so the pressure is fixed at 1.013 bar. Temperature is fixed at 723K. The earlier analysis identified that this temperature maximises purity and gives close to maximum yield at this pressure.

Fig. 6 shows the effect of CaO/C ratio in SE-CLSR. According to the stoichiometry (Table 3), CaO/C = 1 provides enough sorbent to capture all of the CO<sub>2</sub>. Increasing CaO beyond this point does not increase the yield (Fig. 6a), but simply increases the net energy balance and expense associated with excess sorbent. For this reason, the amount of sorbent is fixed at CaO/C = 1.



**Fig. 6** - Effect of sorbent in SE-CLSR of bio-oil at 1.013 bar and 723K, with NiO/C = 1 (a) mass yield, moisture-free basis (b) net process energy balance.

The effects of NiO/C ratio and S/C ratio are illustrated in Fig. 7. Fig. 7b shows that the net energy balance can be reduced by increasing NiO/C ratio, as more heat is released from the oxidation of fuel and Ni. Above a certain NiO/C ratio, autothermal operation ( $\Delta H \leq 0$ ) is theoretically possible. However, the reduced energy balance comes at the cost of lower H<sub>2</sub> yield (Fig. 7a). Similarly, lower S/C ratio reduces heat demand, but also decreases H<sub>2</sub> yield and purity. For S/C = 1, the purity is considerably reduced due to methanation. The selection of NiO/C ratio and S/C ratio should balance the conflicting objectives.



**Fig. 7** - Effect of OTM in SE-CLSR of bio-oil at 1.013 bar and 723K, with CaO/C = 1 (a) mass yield, moisture-free basis, (b) net energy balance, (c) hydrogen purity.

Table 4 shows the autothermal point for the bio-oil surrogate mixture, as well as the model compounds acetic acid and furfural at 723K. In autothermal SE-CLSR of bio-oil, CO<sub>2</sub> and CO are reduced to a negligible level, so that downstream purification requirements are minimised.

A low quantity of steam (S/C = 1) allows a small NiO inventory in autothermal operation, but also supports methanation, so that H<sub>2</sub> purity is low and over 12 mol% of the product gas is CH<sub>4</sub>. By increasing the S/C ratio to 2, autothermal operation can be achieved alongside a high yield (13.6 wt%) and minimal methanation.

When comparing feedstocks, it is notable that the optimal solution for a bio-oil mixture is different to that of the model compounds. As seen in earlier results, furfural is a closer match to bio-oil and thus is a more suitable model compound for understanding thermodynamic potential. However, process development should aim to consider realistic bio-oil mixtures wherever possible.

**Table 4 - Parameters for autothermal operation in SE-CLSR of bio-oil, acetic acid and furfural at 1.013 bar, 723K, with CaO/C = 1. In all cases, solid carbon and CO are negligible (<1ppm)**

Feedstock	S/C	Minimum NiO/C	Yield (wt%, m.f.)	Yield (wt%, wet)	H <sub>2</sub> purity (mol%)	CO <sub>2</sub> (mol%)	CH <sub>4</sub> (mol%)
Bio-oil	3	1.050	11.2	8.51	99.95	0	0.0536
	2	0.785	13.6	10.3	99.52	0	0.482
	1	0.419	11.3	8.59	87.91	0	12.1
Acetic acid	3	1.210	5.31	-	99.94	0.0633	0
	2	0.949	7.04	-	99.99	0	0
	1	0.679	8.49	-	98.86	0	1.14
Furfural	3	0.940	11.1	-	99.91	0.0189	0.0756
	2	0.675	13.6	-	99.43	0.0153	0.552
	1	0.267	9.22	-	80.36	0	19.6

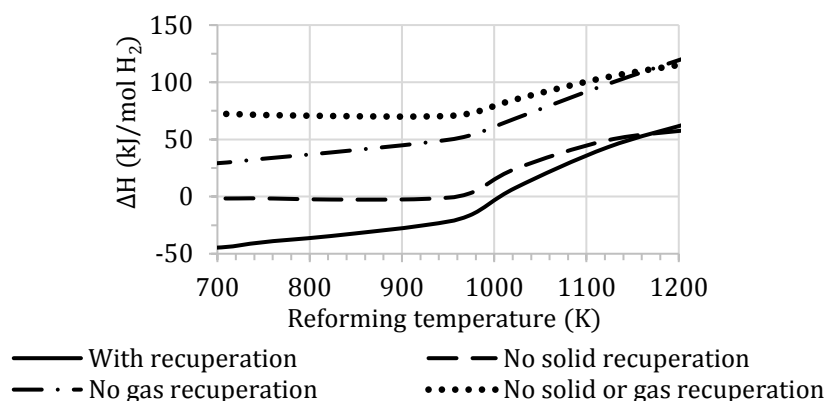
While it may be possible to design an autothermal process, this comes at the expense of a reduced yield (Fig. 7). Hence the preferred operating regime will depend on whether autothermal operation is a priority, which will depend on plant-specific constraints such as required capacity, and the availability and cost of heat. Further techno-economic analysis would be required to find the optimal solution for a given plant, but the above method of thermodynamic analysis could be a valuable starting point for such an evaluation.



#### 4.5. Heat recuperation

The analysis above assumes that usable heat is recovered from both solids and gases after the oxidation/regeneration stage. Fig. 8 shows the impact on the energy balance if the heat recuperation terms are not included. Recuperation of heat from the gas has the largest impact. The impact of heat recuperation from solids decreases when the temperature of reduction/reforming approaches the same temperature as regeneration/oxidation (1170K). When combined, both types of recuperation reduce the net energy balance by 60 to 115 kJ mol<sub>H<sub>2</sub></sub><sup>-1</sup>.

This highlights the importance of heat integration in SE-CLSR. As the process is cyclical, parts of the process are repeatedly heated and cooled, and there is the potential to waste a large amount of heat if process design does not consider heat integration. Previous work has highlighted that the catalyst support can introduce a large additional heating burden[41], which would further increase the impact of heat recuperation from the solids.



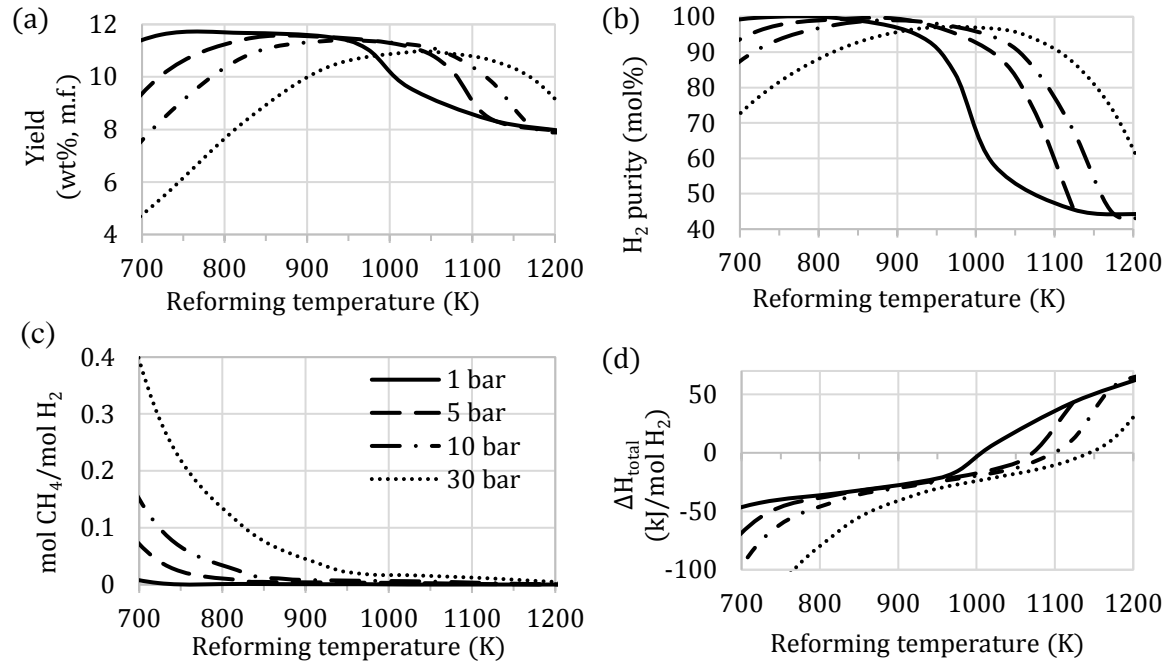
**Fig. 8** - Effect of heat recuperation in SE-CLSR of bio-oil at 1.01325 bar, with S/C = 1, CaO/C = 1, NiO/C = 1.

#### 4.6. The effect of pressure on SE-CLSR

Low pressure favours the production of hydrogen in the steam reforming reaction. However, industrial reforming processes are typically operated at high pressures, in the region of 20 bar or higher, to enable efficient processing of large gas flows in reduced reactor and pipe volumes [74]. Fig. 9 illustrates how the various reforming processes are affected by elevated pressures.

As pressure is increased, the maximum H<sub>2</sub> yield is slightly decreased, and occurs at a higher temperature. At atmospheric pressure, the maximum yield is 11.6 wt% at 723K. At 30 bar, maximum yield is 10.9 wt% at 1023K (Fig. 9a). Fig. 9b shows that purity over 90 mol% is achievable at all the studied pressures, due to the CO<sub>2</sub> sorbent. However, as pressure increases the maximum purity is lowered, and the region of maximum purity is narrowed. In a 30 bar system, H<sub>2</sub> purity peaks at 96.7 mol%. The main impurity is CH<sub>4</sub> (1.8 mol%), as the high pressure system is favourable for methanation (R4 and R5). The level of methanation is illustrated in Fig. 9c.

To achieve a given H<sub>2</sub> yield, the high pressure system requires a higher reformer temperature. However, Fig. 9d shows that the net process energy balance remains similar. In the low temperature region, higher pressure leads to more methanation (Fig. 9c), which releases heat into the reformer. In the high temperature region, the energy balance is affected by the sorption reaction – as the sorbent becomes ineffective, it no longer provides heat for sorption. This effect is observed at lower temperatures in low pressure systems.



**Fig. 9** - Effect of pressure in SE-CLSR of bio-oil, with S/C = 2, NiO/C = 1, CaO/C = 1 (a) mass yield, moisture-free basis, (b) hydrogen purity, (c) methane production, (d) net process energy balance.

Table 5 gives parameters for autothermal operation at elevated pressures. Autothermal operation remains a possibility at industrial reforming pressures, but the higher pressure leads to a higher NiO inventory, reduced yield, and more impurities.

<b>Table 5 - Parameters for autothermal operation in SE-CLSR of bio-oil, at various pressures with CaO/C = 1. In all cases, solid carbon yield is negligible.</b>									
Pressure (bar)	S/C (-)	T (K)	Minimum NiO/C	Yield (wt%, m.f.)	Yield (wt%, wet)	H <sub>2</sub> purity (mol%)	CO (mol%)	CO <sub>2</sub> (mol%)	CH <sub>4</sub> (mol%)
30	3	973	1.189	9.68	7.36	98.7	0.183	0.795	0.367
	2	973	0.867	11.8	8.95	96.9	0.197	0.346	2.57
	1	973	0.424	8.19	6.23	77.6	0.341	0.227	21.9
10	3	873	1.134	10.3	7.82	99.5	0.0580	0.232	0.232
	2	873	0.835	12.6	9.55	98.3	0.0469	0.0939	1.60
5	1	873	0.418	9.20	6.99	81.5	0.0531	0.0531	18.4
	3	848	1.122	10.5	7.96	99.7	0	0.171	0.114
	2	848	0.834	13.0	9.85	99.1	0.0456	0.0917	0.779
	1	848	0.427	9.94	7.55	84.1	0.0507	0.0507	15.8

## 5. Conclusion

A thermodynamic evaluation has demonstrated the potential of bio-oil steam reforming and highlighted the role of advanced reforming techniques in enhancing its performance. Sorption

enhancement can increase hydrogen yield and purity, while also decreasing the net process energy balance. Chemical looping reduces energy balance, although hydrogen yield is reduced due to the partial oxidation of the feedstock. When both techniques are combined in SE-CLSR, bio-oil can be converted to hydrogen in a process with purity over 99% and a low net energy balance.

A PEFB bio-oil surrogate mixture has been compared to model compounds acetic acid and furfural. Due to the similarity in molecular formula, furfural is a more representative model compound for whole PEFB bio-oil. The comparison also highlighted that the feedstock has a considerable impact on process energy balance, and as such process design should consider the variability of bio-oil compositions.

The SE-CLSR of bio-oil can achieve autothermal operation with yields over 13wt% and purity over 99.5 mol%, so that it may be possible to develop small bio-oil reforming plants which are energy self-sufficient and require minimal product purification. Autothermal operation is also achievable at industrial reforming pressures, although the product yield and purity are reduced. The recuperation of heat from solid materials and waste gases is a major contributor to the energy balance. Heat integration is therefore a key consideration for process development.

Carbon deposition is present when S/C ratio is low ( $S/C = 1$ ), but the risk of carbon product can be reduced by increasing the quantity of OTM or sorbent. The autothermal operating regimes for SE-CLSR showed no solid carbon in the equilibrium products.

Thermodynamic analysis demonstrates how advanced reforming techniques can improve the potential of bio-oil as a low-carbon feedstock for hydrogen, in theory improving cost-effectiveness and flexibility of scale in low carbon hydrogen production. This study used a high-level overview of reactor thermodynamics, but further work is required to assess the feasibility of a real process, taking into account practical aspects such as auxiliary units, heat transfer, and the approach to heat integration. Economic constraints are another important consideration. Further process development is required, including the use of techno-economic analysis to evaluate economic feasibility and optimisation.

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### **Declarations of interest**

The authors declare no conflict of interest.

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