Thermodynamic investigation of waste cooking oil based hydrogen generation system with chemical looping process

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Abstract

The thermodynamic features of hydrogen production via chemical looping reforming of waste cooking oil were studied at atmospheric pressure using Gibbs free energy minimization, accounting for the possibility of coke formation. The synthesis gas composition was determined as a function of reforming temperature (400–1000 °C), steam to carbon ratio (S/C, 1–14) and NiO to carbon ratio (NiO/C, 0–2). To evaluate the thermodynamically plausible products, the study started with an expanded product set of approximately 30 by-products. The results show that coke formation can be thermodynamically inhibited by increasing the S/C ratio and/or the NiO/C ratio. The conditions that maximize hydrogen production, minimize methane and carbon monoxide content as well as avoid coke formation at thermoneutral conditions were found to be S/C = 5, T = 600 °C and NiO/C = 0.493. Under these conditions, a hydrogen yield of 144.3 mol/kg of soybean waste cooking oil can be obtained, which appears to be an attractive result for starting experimental research.

1. Introduction

Increasing energy demand coupled with the depletion of fossil fuel resources and increasing environmental pollution has stimulated increasing interest in using H2 as a clean fuel. In fact, H2 has been proposed as a potential energy source due to its abundance, cleanliness and high energy yield. Unfortunately, the majority of H2 is produced from fossil fuels; only 4% of H2 is derived from other renewable sources (Parthasarathy and Narayanan, 2014). Because fossil fuels will be depleted by 2050, it is prudent to search for a sustainable and eco-friendly source of H2 generation (Ashekuzzaman and Jiang, 2014). Renewable technologies to produce H2 for fuel cell applications not only safeguard the environment but also provide a sustainable source of H2.

Among the various H2 production methods, chemical looping reforming (CLR) seems to be a promising and environmentally friendly alternative (de Diego et al., 2009). In fact, CLR has been considered an alternative to catalytic autothermal steam reforming (de Diego et al., 2009; Ortiz et al., 2011). The main advantage of the CLR route is that the oxygen carrier (OC) is an oxide (usually a metal oxide (MeO)) (Proll

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As a result, air may be used instead of pure O₂, and N₂ is never mixed with H₂. A CLR system consists of two interconnected reactors, designated the air (AR) and fuel reactors (FR) (Dueso et al., 2012). In the FR, fuel and steam are burned with an OC to form a synthesis gas (SG) (mixture of CO, H₂, CO₂, CH₄, H₂O, etc.) while OC particles are reduced to a metal (Me). The reduced metal is transferred into the AR, where it is oxidized with air. The regenerated material is then ready to start a new cycle. The major advantage of this process is that the heat needed for converting fuel to H₂ can be supplied without costly O₂ production, without mixing air with carbon containing fuel gases and without using part of the H₂ produced in the process (de Diego et al., 2009). A N₂-free gas stream containing concentrated H₂ and CO is obtained from the reformer, avoiding dilution of the H₂ with N₂. If the H₂ produced is to be used in fuel cells, it should be noted that the dilution of the H₂ stream by N₂ results in an increased anode overpotential during the operation of a proton exchange membrane fuel cell (PEMFC) (da Silva et al., 2012). H₂ production via CLR of various fuels is currently being investigated intensively, and several papers on this subject have already been published. Moldenhauer and co-workers (Moldenhauer et al., 2012) performed a reaction between a nickel-based OC and liquid kerosene in a CLR reactor with continuous particle circulation. An injection system was constructed in which sulfur-free kerosene was evaporated, mixed with superheated steam and fed directly into a lab scale CLR reactor. Moldenhauer et al. showed that it is possible to use liquid fuel in a continuous CLR process and to achieve nearly complete fuel conversion. Kai et al. (Kai et al., 2012) implemented a process of separating H₂ from SG through the chemical looping of a Fe-based catalyst as an oxygen-transfer material and a modified calcium oxide (CaO) as a CO₂ sorbent in a fixed-bed reactor. Kai et al. achieved a hydrogen purity above 99.5% and a yield approaching 27.91 mmol/g Fe catalyst.

Due to the emergence of various food industries, restaurants all over the world, the amount of waste cooking oil (WCO) required for disposal is a major concern. Currently, about 29 million tons of WCO are generated annually in the world (Maddikeri et al., 2012). The base materials of WCO are plant-based lipids, such as soybean oil, corn oil, palm oil, or animal-fats. Chemically, the major components of WCO are triglycerides (tristearin, trimyristin, tripalmitin, tripalmitoleic, trioleate, etc.), with minor amounts of mono and diglycerides (Dale et al., 2008). Until recently, WCO was a significant environmental problem, and the management of this waste was a significant challenge. However, WCO cannot be discharged into sewers as its discharge will lead to blockages, odor or vermin problems and may also pollute watercourses, causing problems for wildlife (Lee et al., 2012). In this context, many scientists have intensively investigated WCO valorization in recent years. The biodiesel production via WCO transesterification remains by far the main route of WCO reuse (Al-Hamamre and Yamin, 2014; Mohammad et al., 2014; Chen et al., 2009). Recently, Amani and co-workers (Amani et al., 2014) investigated the transesterification of waste cooking palm oil with methanol into fatty acid methyl esters (FAMEs) using solid acidic mixed oxide catalysts MnₓZr₀.₅AlₓO₃ prepared via coprecipitation. The authors showed that the catalyst achieved a FAME content of more than 93%, and the optimal reaction conditions were as follows: reaction temperature of 150 °C, reaction time of 5 h, molar methanol-to-WCPO ratio of 14:1, and catalyst loading of 2.5 wt.%. Hamze et al. (Hamze et al., 2015) studied the transesterification of the WCO with response surface methodology (RSM) based on Box–Behnken design. The results revealed that the catalyst concentration is the most important parameter and the maximum biodiesel yield under the optimized conditions was 99.38 wt.%. It should be noted, here, that even with all the advantages, there are still some disadvantages associated with the use of biodiesel in combustion engine. Biodiesel has a 12% lower energy content than fossil diesel, which leads to an increase in fuel consumption of approximately 2–10% (Atabani et al., 2012). Moreover, biodiesel has higher cloud and pour points as well as higher nitrogen oxide emissions than fossil diesel. Biodiesel also has lower volatilities, which lead to soot formation in engines due to incomplete combustion (Atabani et al., 2012). In the past few years, some researchers have turned their interest toward fatty material-based H₂. Converting WCO into H₂ is a three-win alternative, simultaneously addressing pollution, food security, and energy security. Various processes have been proven theoretically and experimentally by many research groups. Pimenidou et al. (Pimenidou et al., 2010a) used a CLR process to produce H₂ from WCO using a nickel-based OC. High purity H₂ was produced by adding calcined dolomite as a CO₂ sorbent into the reactor catalytic bed (Pimenidou et al., 2010b). Dupont et al. (Dupont et al., 2007) studied a novel process of H₂ production called unmixed steam reforming (USR) using methane and sunflower oil. Dupont et al. showed that both methane and sunflower oil are suitable fuels for the USR process and that the thermal decomposition of the fuel played a significant role in early H₂ production concurrent with coking conditions.

This paper explores an innovative application of soybean WCO (SWCO) for H₂ production via a CLR process. We believe that SWCO is a promising feedstock for renewable H₂ production because of SWCO's low O₂ content and high potential yield of H₂. Moreover, SWCO is a potential alternative for H₂ production due to its highly centralized generation in restaurants, various eating outlets and food industries as well as its historically low prices. SWCO may therefore have energy, environmental, and economic advantages that could be exploited. H₂ obtained from SWCO has been proposed to be a low-risk end use for SWCO derived from livestock that have been removed from the food chain. Because of the complex chemical structure of SWCO, the unavailability of physical and chemical properties and the multitude of chemical reactions that can occur, no thermodynamic investigation of H₂ production by CLR of SWCO has been considered in the past. Generally, an investigation of thermodynamic equilibrium is an important tool preceding experimental work. This investigation identifies thermodynamically favorable process operating conditions and predicts the equilibrium product composition. In addition, this investigation is an aid in reactor modeling, in examining kinetic schemes and reaction mechanisms, and in identifying rate-controlling processes (Shi et al., 2001). This paper aims to identify thermodynamically favorable operating conditions at which SWCO may be converted to H₂ by CLR. An expanded product set is used to examine the plausible appearance of the various species in the CLR system. Coke deposits are also investigated to determine coke forming and coke-free regions. It should be noted that the thermodynamic equilibrium investigation conducted here did not consider any kinetic constraints such as
concentration and/or temperature gradients occurring in the process. However, these results are still helpful in locating ranges of favorable operation conditions for the CLR system. Further refinement of the optimal conditions will require kinetic investigations.

2. Hydrogen production by chemical looping reforming of SWCO

2.1. SWCO characterization

SWCO was selected for the case study. Soybean oil (SO) represents 28% of the total vegetable oils (VO) produced in the world, more than rapeseed oil (15%) and less than palm oil (34%) (United States Department of Agriculture, 2012). However, SO production is distributed unevenly around the world, with China, USA, Argentina and Brazil as the top producers (27%, 19%, 17% and 16%, respectively). SO is produced (4%) and consumed (3%) at low levels in Europe. In Tunisia, SO represents about 80% of the imported VO and 65% of the consumed VO; the remainder consists of olive oil, which is not used for frying. During the frying process, VO is heated to approximately 180 °C for relatively long periods in the presence of light and air (Kulkarni and Dalai, 2006). This causes VO degradation, leading to changes in the physico-chemical properties of the oil and resulting in unsuitable oils after some time. Among the most common alterations are changes in color and increases in viscosity, free acid content, specific heat, and foaming tendency (Kulkarni and Dalai, 2006; Permanyer et al., 1985). The present work investigates a SO collected after 8 h of use. Tables 1 and 2 gives the fatty-acid composition of the SWCO considered in this work.

During the thermodynamic investigation of H2 production by CLR of SWCO, the composition of the SG was determined using a simulation to minimize the Gibbs free energy of the SG (Morad et al., 2000; Goodrum and Deller, 2002). All data required to regress the property method were obtained by inserting into the Aspen Plus dialog box (Aspen Technology, Inc., Burlington, MA, USA). All triglyceride forms (e.g., tristearin, trimyristin, tripalmitin, tripalmitoleic, trioleate, tristearin and trilinolenic) are not included in the Aspen Plus™ database and needed to be added before the simulation could be started. This operation required various data, including the chemical structure, normal boiling point, temperature-dependent vapor pressures and heat capacity, molecular weight, standard enthalpy and Gibbs free energy of formation of these compounds, to be inserted into the Aspen Plus™ dialog box (Aspen PlusTM, 1988). All data required to regress the property method were obtained from different literature sources (Yenumula and Maity, 2011; Morad et al., 2000; Goodrum and Deller, 2002).

2.2. Chemical looping reforming of SWCO

A CLR process can be achieved in various ways. As reported in the literature (Ryden et al., 2013), the most commonly proposed processes use circulating fluidized beds (CFB) with OC particles as the bed material. As described in Fig. 1, the CLR of the SWCO system consists of two interconnected fluidized bed reactors, designated as AR and FR.

In the FR, the OC (MeO) is reduced to a metal (Me), and O2 is transferred from the metal oxide to the fuel. The reduced metal is then transferred into the AR, where it is oxidized with air. The material is thus regenerated and ready to start a new cycle. The oxidation reaction of the metal in the AR is very exothermic, whereas the reduction reactions and steam reforming in the FR are endothermic. So, the heat for the endothermic reactions is provided by circulating solids coming from the AR at higher temperature. The heat generated in the AR must be high enough to fulfill the heat balance in the system (Ortiz et al., 2011).

The selection of a suitable OC is a key issue for the large-scale application of CLR technologies. The OC must have sufficient O2 transport capacity, high reactivity under alternating reducing and oxidizing conditions, low tendency for carbon deposition, avoidance of agglomeration, high

| Table 1 – Fatty-acid composition of SWCO (% molar) (Izbaim et al., 2009). |
|------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Formula                | Trilinolenin | Trioleate | Tripalmitin | Trilinolenin | Tristearin |
| Composition (% mol)    | C57H92O6    | C57H104O6 | C51H98O6    | C57H92O6    | C57H110O6   |
| Average molecular composition | C56.28H99.62O6 | C56.28H104.62O6 | C50.12H98.62O6 | C56.28H98.62O6 | C56.28H102.62O6 |

| Table 2 – Synthesis gas composition (% mol) and moles C (graphite), Ni, NiO/kg SWCO in feed for different S/C ratio, T = 300 °C and P = 1 atm. |
|------------------------|------------------------|------------------------|
| Species                | S/C = 0.5              | S/C = 1                 | S/C = 5                 |
| H2O                    | 57.76                  | 60.05                  | 86.36                  |
| CO                     | 18.68                  | 17.27                  | 4.45                   |
| CO2                    | 2.49 × 10⁻²            | 2.27 × 10⁻²            | 4.95 × 10⁻³            |
| H2                     | 3.14                   | 3.23                   | 3.92                   |
| CH4                    | 20.39                  | 19.42                  | 5.27                   |
| Tripalmitin            | –                      | –                      | –                      |
| Tristearin             | –                      | –                      | –                      |
| Trilinolenin           | –                      | –                      | –                      |
| Triglycerides          | –                      | –                      | –                      |
| Ethylene (C2H4)        | 8.42 × 10⁻¹⁰           | 6.89 × 10⁻¹⁰           | 9.33 × 10⁻¹²           |
| Propane (C3H8)         | 7.41 × 10⁻¹³           | 5.90 × 10⁻¹³           | 6.58 × 10⁻¹⁵           |
| n-Butane (C4H10)       | 1.60 × 10⁻¹⁰           | 1.22 × 10⁻¹⁰           | 3.68 × 10⁻¹⁷           |
| Isobutane (C4H10)      | 1.81 × 10⁻¹⁰           | 1.37 × 10⁻¹⁰           | 4.15 × 10⁻¹⁷           |
| 1-Butene (C4H8)        | 1.32 × 10⁻¹⁷           | 9.77 × 10⁻¹⁸           | 2.43 × 10⁻²⁰           |
| 2-Isobutene (C4H8)     | 2.54 × 10⁻¹⁷           | 1.66 × 10⁻¹⁰           | 4.15 × 10⁻¹⁷           |
| 2-Trans-butene (C4H8)  | 3.12 × 10⁻¹⁷           | 2.30 × 10⁻⁰            | 5.74 × 10⁻²⁰           |
| Isobutylene (C4H8)     | 7.58 × 10⁻¹⁷           | 5.61 × 10⁻¹⁷           | 1.39 × 10⁻¹⁹           |
| Methanol (CH3OH)       | 7.35 × 10⁻⁰⁹           | 7.08 × 10⁻⁰⁹           | 2.27 × 10⁻⁰⁹           |
| Formaldehyde (CH2O)    | 6.68 × 10⁻¹⁰           | 6.27 × 10⁻¹⁰           | 1.66 × 10⁻¹⁰           |
| Ethanol (C2H4O)        | 2.3 × 10⁻¹²            | 2.06 × 10⁻¹²           | 1.48 × 10⁻¹³           |
| Acetaldehyde (C2H4O)   | 5.14 × 10⁻¹¹           | 4.47 × 10⁻¹¹           | 2.46 × 10⁻¹²           |
| Acetic acid (C2H4O2)   | 1.58 × 10⁻⁰⁹           | 1.39 × 10⁻⁰⁹           | 9.72 × 10⁻¹⁰           |
| Acetone (C3H6O)        | 1.18 × 10⁻¹³           | 9.57 × 10⁻¹⁴           | 1.26 × 10⁻¹⁵           |
| Glycerol (C3H8O3)      | 1.25 × 10⁻⁰⁹           | 1.06 × 10⁻⁰⁰           | 1.26 × 10⁻¹⁵           |
| Acrolein (C3H4O)       | 3.18 × 10⁻¹⁷           | 2.49 × 10⁻¹⁷           | 2.71 × 10⁻¹⁹           |
| Allyl alcohol (C3H6)   | 2.64 × 10⁻¹⁰           | 2.13 × 10⁻¹⁰           | 2.81 × 10⁻²³           |
| Isopropyl alcohol      | 3.78 × 10⁻¹⁶           | 3.13 × 10⁻¹⁶           | 5.02 × 10⁻¹⁸           |
| n-Butanol (C4H10O)     | 5.16 × 10⁻²²           | 3.96 × 10⁻²²           | 1.42 × 10⁻²⁴           |
| Methyl ethyl Ketone    | 6.17 × 10⁻¹⁸           | 4.62 × 10⁻¹⁸           | 1.36 × 10⁻²⁰           |
| Ethane (C2H6)          | 4.15 × 10⁻¹⁰           | 3.66 × 10⁻¹⁰           | 2.21 × 10⁻⁰⁶           |
| C (Graphite)           | 1.9                    | –                      | –                      |
| Ni                      | 4.26                   | 3.37                   | 1.34                   |

NiO/C ratio is adjusted to obtain reactor temperature of 300 °C at adiabatic condition.
mechanical and chemical stability for successive cycles in a fluidized-bed system, and high conversion of CO and H₂ (Dueso et al., 2010). Several works have explored different OCs for CLR, including nickel, copper, iron, and titanium (Abad et al., 2007; de Diego et al., 2008; García-Labiano et al., 2006; Ishida et al., 2005). As an OC, NiO exhibited a high reaction rate and high fuel conversion of CO and H₂. On the other hand, the Fe₂O₃, CuO, and Mn₂O₃-based OC suffered from poor selectivity and thus produced CO₂, H₂O. Accordingly, NiO was selected as the OC for this investigation.

This study was performed at atmospheric pressure because previous investigations of CLR systems showed that high pressure reduces the theoretical performance, mainly due to lower conversion of fuel (Ryden and Ramos, 2012). The product composition of the CLR and the heat of overall reaction were calculated under conditions that minimize the Gibbs free energy using the UNIF-LBY equation of state. The Aspen Plus™ simulations were set up with a stream class of MIXCIPSD (Aspen PlusTM, 1988), to allow for separation between solids and gases. The method of thermodynamic analysis by minimization of Gibbs free energy used in this investigation has been introduced in our previous papers (Hajjaji and Pons, 2013; Hajjaji et al., 2013) and has also been described in detail by other groups (Wang et al., 2009, 2012; Wang, 2011).

The main reactions involved in the AR and FR reactors are the following.

Air-reactor

Ni + 0.5SO₂(air) → NiO( + N₂)  \[ \Delta H_{298K} = -239.70kJ/mol \]  (1)

Fuel-reactor

\[ \text{C}_{66.28}\text{H}_{99.62}\text{O}_6 + 50.28\text{NiO} \rightarrow 56.28\text{CO} + 49.81\text{H}_2 + 50.28\text{Ni} \]
\[ \Delta H_{298K} = 7.54MJ/mol \]  (2)

\[ \text{C}_{66.28}\text{H}_{99.62}\text{O}_6 + 56.28\text{CO}_2 + 49.81\text{H}_2O + 56.28\text{Ni} \]
\[ \Delta H_{298K} = 2.89MJ/mol \]  (3)

\[ \text{C}_{66.28}\text{H}_{99.62}\text{O}_6 + 106.56\text{H}_2O \rightarrow 56.28\text{CO}_2 + 156.37\text{H}_2 \]
\[ \Delta H_{298K} = 7.70MJ/mol \]  (4)

H₂ + NiO ↔ H₂O + Ni  \[ \Delta H_{298K} = -2.12kJ/mol \]  (5)

CO + NiO ↔ CO₂ + Ni  \[ \Delta H_{298K} = -43.29kJ/mol \]  (6)

Water gas shift (WGS):

CO + H₂O ↔ CO₂ + H₂  \[ \Delta H_{298K} = -41.17kJ/mol \]  (7)

Methanation:

CO + 3H₂ ↔ CH₄ + H₂O  \[ \Delta H_{298K} = -206.11kJ/mol \]  (8)

CO₂ + 4H₂ ↔ CH₄ + 2H₂O  \[ \Delta H_{298K} = -164.94kJ/mol \]  (9)

Carbon formation:

\[ \text{C}_{66.28}\text{H}_{99.62}\text{O}_6 + 43.81\text{NiO} \rightarrow 56.28\text{C} + 49.81\text{H}_2O + 43.81\text{Ni} \]
\[ \Delta H_{298K} = -2.02MJ/mol \]  (10)

2CO ↔ CO₂ + C  \[ \Delta H_{298K} = -172.43kJ/mol \]  (11)

CH₄ ↔ 2H₂ + C  \[ \Delta H_{298K} = 74.85kJ/mol \]  (12)

CO + H₂ ↔ C + H₂O  \[ \Delta H_{298K} = -131.26kJ/mol \]  (13)

The overall reaction of FR can be expressed as Eq. (14), a combination of the aforementioned reactions.

\[ \text{C}_{66.28}\text{H}_{99.62}\text{O}_6 + a\text{NiO} + b\text{H}_2\text{O} + c\text{CO} + d\text{CO}_2 + e\text{H}_2 + f\text{CH}_4 + g\text{C} + h\text{Ni} \]
\[ \Delta H_{298K} \]  (14)

The stoichiometric coefficients \((a-h)\) depend on the reformer temperature (T), pressure (P), the steam to carbon molar ratio \((S/C)\) ratio and the NiO to carbon molar ratio \((\text{NiO}/\text{C})\).

The \(S/C\) ratio is given by Eq. (15) (Yenumala and Maity, 2011).

\[ \text{Steam} \to \text{carbon ratio} = \frac{\text{moles of steam}}{\text{moles of SWCO}} \times \frac{\text{moles of steam}}{\text{moles of SWCO}} = \frac{(\text{moles of steam})}{106.56} \times (\text{moles of SWCO}) \]  (15)

The NiO/C ratio is given by Eq. (16)

\[ \text{NiO} \to \text{carbon ratio} = \frac{\text{moles of NiO}}{\text{moles of SWCO}} \times \frac{\text{moles of NiO}}{\text{moles of SWCO}} = \frac{(\text{moles of NiO})}{50.28} \times (\text{moles of SWCO}) \]  (16)
The stoichiometric number of moles of steam and NiO are given by reactions Eq. (4) and Eq. (2), respectively. Simulations were run with varying S/C and NiO/C ratios as well as varying temperatures to maximize H₂ production while minimizing CO and CH₄ content in the SG and preventing coke formation. It is important to reduce the CO concentration in the SG to reduce the required size of the gas cleaning unit (Water Gas Shift (WGS) and purification). Additionally, for H₂ production, it is clear that CH₄ is not a desirable product, as the formation of CH₄ competes with H₂ production.

The CLR reactor suggested in this investigation (Fig. 2) is very similar to the CLR system reported by Rydén et al. (Rydén and Ramos, 2012) and Yahom et al. (Yahom et al., 2014). The system consists of a FR, an AR, CYCLONE1, CYCLONE2 and two heat exchangers (HX1 and HX2). The inlet streams (water and SWCO) enter the FR as vapor by means of two heat exchangers (HX1 and HX2). The preheat temperature for the water steam was set at 130 °C to avoid film boiling and to maximize heat transfer (Pimenidou et al., 2010a). A preheat temperature of 300 °C was selected to bring the SWCO as close as possible to vaporization while avoiding thermal decomposition to prevent tar formation prior to contact with the catalyst (Pimenidou et al., 2010a). The Aspen Plus™ library model HEATER was used for the two heat exchangers with one input and output stream. The FR was modeled as an isothermal reactor using the library model RGibbs (Salemme et al., 2010). The RGibbs reactor of the Aspen package was selected to calculate chemical and phase equilibria by minimizing the Gibbs free energy of all of the species expected to participate in the equilibrium. The FR product stream (flux 5) is transported to CYCLONE1 to separate the Ni solid from the SG (flux 6). The Ni solid (flux 7) is transferred to the AR for oxidation with air (flux 11), forming NiO. The AR was modeled as an adiabatic reactor using the library model Rstoic. RStoic is used when the reaction stoichiometry and degree of conversion are known while the reaction kinetics are either unknown or irrelevant (Salemme et al., 2010). The mixture obtained (flux 8) is introduced into CYCLONE2 to separate N₂, O₂ and NiO. The two cyclones were modeled using the Aspen Plus™ library model cyclone.

3. Results and discussion

3.1. Chemical looping reforming of SWCO: thermodynamically possible products

CLR of SWCO involves a complex reaction system with several undesired reaction paths. The main species involved in the FR product are H₂, CH₄, CO₂, CO, H₂O, C(graphite), NiO and Ni. Depending on the operating conditions, the product distribution in the FR product may be different from the distribution described above. In this paper, equilibrium compositions were calculated by minimizing the Gibbs free energy with the aid of Aspen Plus™ software. This software requires the input of all possible chemical species present in the system as reactants and products (Rydén et al., 2013). Therefore, the standard product set was expanded to include these possible products; this expanded product-set is given in Table 3.

Table 3 shows that triglycerides are fully converted and that the concentrations of ethane, ethylene, acetylene and other oxygenated compounds in the product stream can be considered thermodynamically unstable products. Therefore, these unstable products were not reported in the present study. These compounds are formed by thermal cracking and then converted by a steam reforming reaction. However, the occurrence of these products in the experimental work is due to the kinetic control of CLR processes in practice. Therefore, the component list for further thermodynamic equilibrium

![Diagram of SWCO chemical looping reforming in Aspen Plus™ program.](image)

![Coke formation boundary of CLR of SWCO as a function of the NiO/C ratio for a range of different S/C ratios at 1 atm.](image)
3.2. Coke formation

Coke formation is a major problem in the CLR process. Coke may encapsulate the catalyst surface or dissolve and diffuse into catalyst pellet, reducing its activity (Annesini et al.). Therefore, coke formation was investigated to determine coke forming and coke-free regions. Operating the CLR in coke-free regions may prevent coke formation, which severely limits the chemical reactions that can occur.

Fig. 3 illustrates the coke formation boundary of CLR of SWCO as a function of the NiO/C ratio for a range of different S/C ratios. For given S/C and NiO/C ratios, the temperature at which the first disappearance of solid carbon ($T_{CD}$) was achieved was considered the carbon boundary. The regions below and above the boundary are the coke forming and coke-free regions, respectively. For a given temperature, it was observed that coke formation is suppressed by an increased NiO/C ratio and/or an increased S/C ratio. Moreover, high temperatures and a high S/C ratio inhibit coke formation. For example, coke formation may be avoided with S/C ratios higher than 1 and temperatures above 300 °C.

It should be noted that the oxygen carrier might influence carbon deposition and therefore requires further investigation. In fact, Jin and co-workers (Jin et al., 1998) investigated a bimetallic CoO–NiO/YSZ system for a chemical looping combustion study. The authors concluded that carbon deposition can be completely eliminated by employing Co as a promoter along with NiO as the main active species on a YSZ support. Jin et al. speculate that the formation of a solid solution between cobalt and nickel might change the free energy of the carbon formation reactions, reducing coke formation.

3.3. Thermodynamic equilibrium

Figs. 4–6 illustrates the investigation of the CLR of SWCO. Fig. 4 shows the amount of hydrogen produced (mole H$_2$/kg SWCO) as a function of S/C ratio and NiO/C ratio at different temperatures. Hydrogen production decreases with increasing NiO/C ratio as expected, with the oxidation reaction (Eq. (3) and Eq. (4)) becoming more dominant with an increasing amount of NiO. In fact, the NiO ratio controls the amount of SWCO retained for oxidation, and the high NiO ratio results in a low amount of SWCO available for the reforming reaction (i.e., a decrease in hydrogen yield). Obviously, if a small amount of oxygen (low NiO ratio) is insufficient to fully convert the SWCO and compensate for the endothermicity of the reforming reaction Eq. (4), a strong excess of NiO (oxygen) burns all of the remaining chemical species, generating CO$_2$ and H$_2$O. At low NiO content and high temperatures, higher hydrogen production is achieved due to the increasing dominance of the endothermic reaction Eq. (4).

Hydrogen production is particularly sensitive to temperature at low NiO/C ratios due to the equilibrium composition of reaction Eq. (4), which shifts further to the left with decreasing temperature. As expected, the results show an increase in hydrogen production with increasing S/C ratio, shifting the
equilibrium composition of the steam reforming reaction Eq. (4) and WGS Eq. (7) to the right. This behavior is consistent with Le Chatelier’s principle, which states that if a dynamic equilibrium is disturbed, the equilibrium shifts to counteract the change. It is notable that the gain in hydrogen productivity is not significant for S/C ratios above 5, where the reaction system consumes excessive amounts of water. Fig. 4 shows that an increase in temperature shifts the equilibrium position of the endothermic reaction Eq. (4) to the right, resulting in an increase in hydrogen production with increasing temperature.

Fig. 5 shows the CO produced per kg of SWCO in the reforming reactor as a function of S/C and NiO/C ratios at different temperatures. The CO content increases with increasing temperature. This is because low temperatures favor the exothermic WGS and methanation reactions (Eq. (7), Eq. (8) and Eq. (9)), leading to low CO content. Simultaneously obtaining high hydrogen content and low carbon monoxide content is contradictory. However, because the amount of hydrogen produced can be reduced at low temperatures, moderately high temperatures are preferred, even though a small amount of CO will be produced. At a given temperature, an increase in the NiO/C and/or S/C ratios decreases CO production. In fact, an increase in the NiO/C ratio shifts reaction Eq. (6) towards the carbon dioxide formation side.

As observed in Fig. 6, at a given temperature, methane yield decreases precipitously as the NiO/C ratio is increased. The amount of methane produced at S/C ratios lower than 5 is relatively higher than the amount produced at ratios higher than 5. However, methane yield decreases as temperature is increased, as low temperatures favor the exothermic methanation reactions (Eq. (8) and Eq. (9)).

In conclusion, high hydrogen yields (green part of Fig. 4), moderate carbon monoxide yield (blue part in Fig. 5), trace amounts of methane (purple part in Fig. 4), and no coke formation can be achieved simultaneously. Hydrogen production via CLR of SWCO can be optimized at temperatures of 600–900 °C, S/C ratio of 3–5, and NiO/C ratios of 0.0–0.6. The NiO/C ratio and reforming temperature should be chosen appropriately to create a thermally self-sustaining system. Further optimum conditions for hydrogen production will be discussed in the following section.

3.4. Thermoneutral condition

In the CLR system, introducing more NiO into the FR promoted exothermic oxidation reactions, reducing the heat duty of the reactor. As a result, it is possible to operate the reactor with no external heat for cooling or heating, making the CLR process valuable from an energy consumption point of view (Kale and Kulkarni, 2010). The operating temperature at which the external heat flow is zero is known as the adiabatic temperature (Kale and Kulkarni, 2010). A thermoneutral investigation is performed by considering SWCO, steam and NiO as feeds to the reactor at reactor temperature. Fig. 7 shows the relationship of heat duty with NiO/C ratio at different temperatures. The NiO/C ratio has a very strong effect on the heat of combustion.
reaction. An increase in the NiO/C ratio can even transform the overall reaction from endothermic to exothermic. At 600 °C, NiO/C ratios of 0.493–0.495 yield thermoneutral conditions with S/C values between 3 and 5. At 900 °C, the NiO/C ratios of 0.487–0.508 yield thermoneutral conditions. For all of the configurations considered, thermoneutrality is obtained with O/C ratios of 0.493–0.525.

Considering the aforementioned interpretations, the recommended conditions found to maximize hydrogen production, minimize methane and carbon monoxide formation and avoid coke formation at thermoneutral conditions are S/C = 5, T = 600 °C and NiO/C = 0.493. Table 3 presents the characteristics of the SWCO CLR reactor under the optimal conditions.

Table 3 shows that 144.3 mol/kg of soybean waste cooking oil can be obtained at recommended conditions, this value is slightly higher (16%) than that experimental results reported in literature for chemical looping reforming of rapeseed waste cooking oil (124.7 mol/kg of rapeseed waste cooking oil) (Pimenidou et al., 2010b).

The energetic performance of a CLR system is conventionally evaluated by the thermal efficiency. The thermal efficiency is based on considerations of the first law of thermodynamics and is calculated as the energy output divided by the energy input (Benito et al., 2007) as shown in Eq. (17).

\[ \eta_{\text{Thermal}} = \frac{m_{H_2} \times LHV_{H_2}}{m_{SWCO} \times LHV_{SWCO} + Q_{HX1} + Q_{HX2}} \]  

where \( m_i \) and LHV, are the mass flow and the Lower Heating Value of species “i”, respectively (LHV_{SWCO} = 40.55 MJ/kg and LHV_{H2} = 120 MJ/kg). \( Q_{HX1} \) and \( Q_{HX2} \) are the heat duty of the heat exchangers HX1 and HX2, respectively.

The thermal efficiency of the CLR system is 48.7%, which indicates that about half of the energy fed into the system is finally recovered in the useful product (H_2).

4. Conclusions

A thermodynamic analysis of the CLR of SWCO was performed at atmospheric pressure via Gibbs free energy minimization, accounting for the possibility of coke formation. The SG composition was determined as a function of reforming temperature, S/C ratio and NiO/C ratio. SWCO was considered to be a mixture of triglycerides consisting of the three fatty acid groups in the SWCO structure. Equilibrium compositions were calculated using Aspen Plus™. Before the simulation was started, triglycerides, the main components of SWCO and non-databank compounds in Aspen Plus™ were added. The study started with an expanded product set of approximately 30 by-products to determine which products were thermodynamically plausible.

The main conclusions that can be drawn from the present study are the following:

- Thermodynamically, CH_4 and C (graphite) are important products that coexist with H_2O, CO_2, CO and H_2, while the formation of by-products such as alkanes containing two or more carbon atoms, acids, alkenes and various alcohols are negligible.
Coke formation can be thermodynamically inhibited by increasing the S/C ratio and/or the NiO/C ratio. Avoidance of coke formation is possible for S/C ratios higher than 1 and temperatures above 300 °C.

Hydrogen production via CLR of SWCO is optimal at temperatures of 600–900 °C, S/C ratio of 3–5, and NiO/C ratios of 0.0–0.6.

- The recommended conditions which maximize hydrogen production while minimizing methane and carbon monoxide contents and avoiding coke formation at thermo-neutral conditions are S/C = 5, T = 600 °C and NiO/C = 0.493.

Finally, under the recommended conditions, a hydrogen yield of 144.3 mol/kg SWCO can be obtained with thermal self-sustaining behavior. This yield suggests the value of further experimental research.

References
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