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Waste lubricating oil as a source of hydrogen fuel using chemical looping steam reforming

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ABSTRACT

Initial results are presented for the production of hydrogen from waste lubricating oil using a chemical looping reforming (CLR) process. The development of flexible and sustainable sources of hydrogen will be required to facilitate a 'hydrogen economy'. The novel CLR process presented in this paper has an advantage over hydrogen production from conventional steam reforming because CLR can use complex, low value, waste oils. Also, because the process is scalable to small and medium size, hydrogen can be produced close to where it is required, minimising transport costs. Waste lubricating oil typically contains 13-14% weight of hydrogen, which through the steam reforming process could produce a syngas containing around 75 vol% H_2, representing over 40 wt% of the fuel. The waste oil was converted to a hydrogen rich syngas in a packed bed reactor, using a Ni/ Al_2O_3 catalyst as the oxygen transfer material (OTM). An oil conversion rate based on carbon species (CO, CO_2 and CH_4)

of up to ~95% was achieved. The steam to hydrogen conversion of 53%, accounted for 63% of the total H_2 produced, compared to the theoretical ideal of 67.4%. The syngas composition was initally >65 vol% H_2, 15 vol% CO, 15 vol% CO_2, and <5 vol% CH_4. Deterioration of the reactants conversion, specifically steam, was observed over repeated cycles indicating fouling of the catalyst. This was not by carbonaceous deposits, which were eliminated during the cycle's alternated oxidation steps, but could be by trace additives within the lubricating oil. Further work is planned in order to overcome this issue.

INTRODUCTION

A major hurdle to greater use of hydrogen as a fuel is that it is largely produced from fossil fuel sources such as natural gas. Close to 95% of the hydrogen produced in the USA is via energy intensive steam reforming of methane at temperatures of 700°C-1000°C [1]. Issues of sustainability and fuel security have led to interest in alternative fuel sources such as bio-fuels and waste derived fossil fuels.

Some 40 million metric tonnes [2] of lubricating oils are annually produced worldwide, 60% of which ending up as waste. Disposal of this waste oil can be achieved by re-refining or combustion. However, as waste lubricating oil typically contains 13-14% weight of hydrogen, which translates into a syngas by steam reforming with ~40 wt % hydrogen content on a fuel basis, or ~12 % on a stoichiometric fuel and steam basis. This indicates that it can be considered as a hydrogen carrier on a par with many advanced hydrogen storage materials.

There are few published studies exploring the use of waste lubricating oil for hydrogen production. Ramasamy and T-Raissi looked at three potential methods of reforming used lube oil to hydrogen [3]. These were: conventional steam reforming, supercritical water gasification and thermolytic cracking. However, the hydrogen yields and purity were low for all methods. A reason for the low yields was the formation of other hydrocarbon species such as methane and ethane. Even at temperatures of 880ºC used for the cracking process, the H_2 in the gaseous products was only ~30 vol%. They also reported issues due to coking with both the steam reforming process and the cracking processes, which led to blockages in the process lines.

Chemical looping steam reforming (CLR) in a packed bed reactor, or 'unmixed' steam reforming, differs from the conventional process in that it involves cycling between fuel-steam feed steps and oxidation steps. The use of a single reactor has advantages of improved energy efficiency, and scalability, enabling the reactor to be sited locally to where the hydrogen is required. Kumar et. al [4] and Lyon and Cole [5] have shown that hydrogen rich syngas can be produced autothermally using this system, when incorporating a CO_2-sorbent. The CLR process used in this study operates on the principle that the Ni-based oxygen transfer material (OTM) can act as a steam reforming catalyst when in its reduced state. Carbonaceous deposits that form during the fuel feed cycle are oxidised during the Ni-OTM re-oxidation cycle, generating additional heat to that of the Ni oxidation reaction. This heat is used to support the steam reforming in the subsequent fuel feed cycle. Previous work by the authors has demonstrated high reactant conversions using fuels such as methane [6], vegetable oil [7] and waste cooking oil [8, 9].

A crucial requirement of the CLR process is that the fuel can reduce the OTM during the beginning of the fuel feed step to enable the steam reforming to start from cycle to cycle. The ability of complex fuels such as lubricating oil to fulfill this function has not been reported in the literature to date. Details of the reactions involved in CLR are shown in the next section.

EXPERIMENTAL

Materials

The specification of the waste lubricating oil used in this study was a 5w/ 40 synthetic oil. The oil had been drained after ~2000 miles usage in a 1.2 L, gasoline-fueled car engine. The density of the oil was 879.8 kg m^{-3}, which correlates with other studies [2, 3]. Analysis of the CHNS content of the oil was obtained using a Flash EA1112 Elemental Analyser by CE Instruments. This gave elemental mass fractions of 84.3 wt% carbon, 13.6 wt% hydrogen and 0.25 wt% nitrogen. No sulphur was detected and the oxygen content was taken by difference to be 1.8 wt%. Thermogravimetric analysis (TGA) was used to obtain the simulated distillation characteristics and proximate analysis of the oil. This was performed on a Shimadzu TGA 50 with TA 60 data collection software. The TGA results were further analysed to enable kinetic modelling of the oil evaporation and decomposition characteristics.

The OTM catalyst used was 18 wt% NiO on Al_2O_3 provided by Johnson Matthey. The material was received in pellet form and was broken and sieved to particle size range of 0.85-2mm prior to use.

Reactor set-up

The experiments were conducted in a quartz, bench-scale reactor as shown in Figure 1. The rates of fuel and steam flows were controlled using syringe pumps (New Era Pump Systems). The gas flows were controlled using MKS mass flow controllers. The composition of the product gas was measured every 5 seconds using Advanced Optima analysers by ABB. Concentrations of CH_4, CO and CO_2 were measured using a Uras 14 infrared absorption analyser , H_2 was measured using a Caldos 15 thermal conductivity analyser and O_2 was measured using a Magnos 106 paramagnetic analyser. For this initial study, no other products were measured.

Test Procedures

CLR was conducted over 6 cycles at atmospheric pressure using a molar steam to carbon ratio (S:C) of 2.5, reactor bed temperature of 600 ºC and 20 g of the Ni-OTM. These conditions resulted in a weight hourly space velocity (WHSV) of 0.77 h^{-1}. The WHSV is the total reactant mass flow rate per unit mass of catalyst in the reactor. The test was preceded by an OTM reduction period using H_2 in order to pre-activate the catalyst. After that the cycles comprised of the fuel/water feed using N_2 as a carrier gas, followed by a N_2 purge, completed by an oxidation step using air. Effectively, 6 cycles were equivalent to 12 reactive steps, not counting the potential reactions during the N_2 purge. It should be noted that in full-scale operation of the process, the N_2 carrier gas and purge period would not be required as this is primarily to facilitate analysis of the chemical processes, and to conduct elemental balances. The elemental balances enable the calculation of the process outputs such as fuel and steam conversions and H_2 yield.

(i) Catalyst activation step (cycle 1 only)

Before the CLR test cycles started, the fresh OTM catalyst was activated by reducing the NiO to Ni using a flow of 5% hydrogen in nitrogen carrier gas at a temperature of 600 °C, resulting in production of steam. The use of hydrogen for this step is in line with the start-up procedure of industrial steam reforming processes, in which an alternative reductant that can be used is methane. The reduction of the catalyst was deemed complete when the measured output gas composition increased from 0 % to the 5% of the feed reducing mixture. In the event that the fuel (i.e. waste oil) could be proven to fully reduce the OTM, then this step could be omitted and the fuel and steam would be fed directly onto to the fully oxidised catalyst.

(ii) Fuel and steam feed step

A flow of 200 cm^3 min^{-1} (STP) of nitrogen as carrier gas was maintained throughout the fuel and steam feed step. The reactor temperature was maintained at 600 °C measured at the top of the catalyst. Fuel and water were simultaneously fed into the top of the reactor, from where they dropped directly into the hot zone.

The reactions occurring during the fuel feed step are summarised below:

Fuel thermal decomposition on NiO bed causes NiO to reduce to Ni (2nd cycle onwards).

This is done via the reaction of 'unmixed combustion':

R1 $C_nH_mO_k + (2n+m/2-k)NiO \rightarrow nCO_2 + (m/2)H_2O+(2n+m/2-k)Ni$ $\Delta H>0$

(This stage produces the most C deposits)

Once Ni sufficiently reduced, steam reforming occurs

R2 $C_nH_mO_k + (n-k)H_2O \rightarrow nCO+ (n+m/2-k)H_2$ $\Delta H>0$
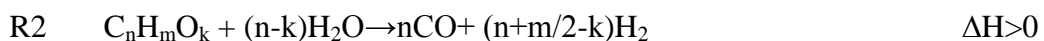
And the water gas shift reaction follows.

R3 $CO+H_2O \leftrightarrow CO_2+H_2$ $\Delta H \rightarrow <0$

It can be seen that the steam reforming reaction is endothermic and so heat is required to maintain the required temperature. It is worthy to note that though reactions R2 and R3

represent the main H_2 production reactions, the maximum contribution of the steam reactant to the H_2 yield is (2n-k) / (2n+0.5m-k), which for our waste lubricant oil ($C_{0.340} H_{0.6532} O_{0.005}$), is 67.4%. The remainder 32.6 % originates from the fuel conversion. This represents a great advantage of the catalytic steam reforming process over other H_2-producing processes such as thermal decomposition or high temperature water splitting processes, in that significant water conversion to hydrogen can be carried out at medium temperatures with high rates by combination with a hydrocarbon.

The reactor was purged with N_2 gas after each fuel step. Sufficient time was allowed to ensure that there was no syngas remaining in the system before the air step commenced. This was verified by monitoring the gas composition.

(iii) Oxidation step: air feed

For the oxidation step, the N_2 gas was switched off and replaced by a flow of air at 1000 cm^3 min^{-1} (STP). This had the effect of re-oxidising the OTM whilst also burning off any coke deposits that form. This stage is exothermic and so the heat produced can be used to support the subsequent fuel-feed step.

R4	$C+O_2 \rightarrow CO_2$	$\Delta H<0$
R5	$C+0.5O_2 \rightarrow CO$	$\Delta H<0$

Ni oxidation on support

R6	$Ni + 0.5O_2 \rightarrow NiO$	$\Delta H<0$

Once completion of the air step was observed by stabilisation of the measured gases, the reactor was again purged with N_2 gas, and then the fuel step was repeated.

Elemental Balances.

The fuel and water fractional conversions, as well as the selectivity of the carbon-containing products, and the hydrogen yield (in mol H_2 per mol of C in the fuel), were calculated from elemental balances using the dry gas composition. It is assumed that fuel conversions of less than 100% based on the carbon balance would indicate the degree of coke formation.

RESULTS AND DISCUSSION

Thermogravimetic Analysis of Oil and kinetics of mass loss.

The proximate analysis of the waste lubricating oil indicated that it was 98.5 wt% volatile matter, 1.4 wt% ash and ~0.1% wt elemental carbon. For this small scale study, the entire oil was fed into the reactor. However, the significant ash content of the oil could eventually affect catalyst performance and so treatment such as pre-vapourisation of the volatile portion of the oil may be required, so that the ash can be minimised. An example of the TGA mass loss curve is shown in Figure 2, which was conducted with a heating rate of 6 °C min^{-1}.

Kinetic modelling of oil.

An improved Coats and Redfern method was used to model the kinetics of the mass loss following the theory of Urbanovici et al [10].

Similar to Gomez-Rico et al's work [2], the mass loss curve required modelling in two stages corresponding to low temperature, low conversion and high temperature, high conversion, with (300 °C, 60% conversion) as the joining point. In the first stage, the best fitting model was found to be a nth order reaction model with order 0 (equivalent to power law order 1), which, with a linear correlation coefficient of 0.9996 generated by the iterative Coats-Redfern method, yielded an activation energy of 57.8 ± 0.6 kJ mol^{-1}. This mass loss was attributed to evaporation of the lighter components. The second stage was fitted with an nth order reaction model with order 2.8, and with a linear correlation coefficient of 0.984, yielded the activation energy of 449 kJ mol^{-1}. This second stage was attributed to thermal decomposition of the heavier components to gaseous products, as investigated by Gomez-Rico et al [2].

Characteristics of a chemical looping reforming cycle: fuel-steam and air feeds

Figure 3 plots the profiles of the dry reformate concentrations in H_2, CO_2, CO and CH_4 with time on-stream for cycle 4, as typically representative of the other cycles.

Two regimes could be identified whereby initially only CO_2 evolved from the reactor for approximately 1000 s via a transient regime, followed by the emergence of H_2 as the main product. CO and CH_4 were measured in the syngas as the steady state of steam reforming was established. As the reactor feed contains the N_2 carrier gas, the difference of the sum of the dry vol. % of the H_2, CO_2, CO and CH_4 gases to 100 % was assumed in the elemental balances to correspond to the unmeasured N_2. This assumption was corroborated by the carbon balance, which indicated lube oil fractional conversions near 1 in both regimes, i.e. accounting for nearly all the carbon products. This demonstrated that concentrations of other unmeasured hydrocarbons must have been extremely low for these conditions.

The ability to derive an accurate N_2 fraction is crucial as it allows determination of the total dry molar flow rate leaving the reactor. This gives the production rates of H_2, and as a result, the H_2 yield and that of the other products. The hydrogen balance then allows the determination of the fractional water conversion, in turn giving evidence of the activities of the steam reforming and water gas shift reactions, as opposed to other routes of hydrogen production such as fuel thermal decomposition. With the onset of steam reforming and the water gas shift reaction, the process of generating hydrogen from the waste lubricating oil is maximised.

Figure 4 plots the fractional lube oil and water conversions with time on-stream for the same cycle as Figure 3. The two reaction regimes are again clearly visible, this time with the indication that steam was consumed in the first regime (negative fractions), and produced in the second (positive fractions), accompanied by a slight increase in average fuel conversion. This was observed in the authors' prior studies of chemical looping reforming of methane [6].

Further data analysis arising from the oxygen elemental balance (not shown), clearly indicates that the first regime consisted of the reduction rate of the NiO present in the reactor bed by the fuel itself, as part of the expected chemical looping reforming process (reaction R1), creating CO_2 and steam as the products. The second regime (t > 2000 s), with its simultaneous consumption of fuel and steam generating H_2 and CO as the products, provides evidence that the steam reforming reaction (R2) and water gas shift (R3) had become

established. This mechanism was observed in all the 6 cycles studied, although at different magnitudes.

Figure 5 illustrates the completion of a typical cycle by plotting the gas profiles during the oxidation/ air feed step. It can be seen that the air feed results first in a short burst of syngas flush, evidenced by the small H_2 peak. This was followed by large and prolonged evolution of CO_2 , with little CO and no oxygen. This was the result of oxidation of the carbonaceous deposits formed during the previous steam reforming step, which, together with the re-oxidation of the Ni, consumed all the oxygen provided by the air feed.

Figure 6 plots the selectivity of the oxygen containing products CO_2 and NiO during the air feed step, which were calculated via a carbon and oxygen balance. It can be seen that the carbon deposit oxidation occurred simultaneously with the Ni oxidation, the latter dominating the consumption of oxygen. This has also been observed in previous studies using waste vegetable cooking oil as the fuel for chemical looping reforming [8,9].

It is promising that the individual reaction steps for a potentially successful chemical looping reforming process are in evidence in these experiments. These are: the ability of the fuel to reduce the oxidised catalyst from a fully oxidised to fully reduced state, the uptake of the oxygen on the Ni-OTM with simultaneous regeneration of the catalyst surface by oxidation of the carbonaceous deposits, and the establishment of a steady state in steam reforming and water gas shift with high fuel and steam conversions, as achieved in the first cycle.

Chemical looping reforming cyclic behavior

Table 1 lists the average outputs of fuel and steam conversion fractions, selectivity of the carbon containing products and the hydrogen yield efficiency (H_2 yield eff). The latter is defined as the ratio of the experimental rate of production of H_2 per mol of carbon in the feed to the maximum theoretical rate of H_2 that would be produced via reactions R2 and R3, not taking into account thermodynamic equilibrium limitations. In the case of this waste lube oil fuel, the theoretical yield was 2.943 mol H_2/mol C in the feed, calculated as $(2n+0.5n-k)/n$ for the '$C_nH_mO_k$' fuel.

In Table 1, X_{oil} is the lubricating oil fractional conversion, X_{H20} is the water fractional conversion, Sel.CO, Sel.CO_2 and Sel.CH_4 are the selectivity of the carbon containing products and 'H$_2$ yield eff.' is the hydrogen yield efficiency defined above.

The H_2 yield efficiency started at 71.2% for the first cycle and dropped to 30.1% at the end of the 6th cycle. The initial difference from 100% in cycle 1 had three causes. Firstly, the temperature of operation of 600 ºC would have caused some reverse water gas shift, as evidenced by the CO selectivity of 43%, which was just under that of CO_2. Secondly, the oil conversion fraction was below 100% (94.4%), thus affecting the H_2 yield. Thirdly, the by-product selectivity of CH_4 was 8.5%, when each mol of CH_4 could potentially have produced four mol of H_2 via steam reforming. The fuel and water conversion fractions along with the hydrogen yield efficiency variation from cycle to cycle are illustrated in Figure 7.

The fractional steam conversion of 53.5% for cycle 1 is considered very good. This corresponded to 63% steam contribution to the H_2 yield, when the theoretical maximum was 67.4%. The steam conversion is also subject to the reverse water gas shift reaction, so could not have fulfilled its full H_2 producing potential, being limited by the equilibrium thermodynamics. However, with the increasing number of cycles, the water conversion was seen to decrease quite dramatically to just 9%. At this point, the reaction regime would have been closer to fuel thermal decomposition than to steam reforming coupled with water gas shift. This is suggestive of a catalyst fouling effect, and we can also see similar but less drastic effects on the slow decrease in lube oil conversion from 95% down to 78% by the sixth cycle. Throughout this deactivation process, the selectivity to the carbon containing products was not affected. Comparing the experimental H_2 yield obtained in the final cycle to that predicted assuming a full thermal decomposition of the fuel (to carbon and H_2 products), very similar amounts were obtained. This corroborated the interpretation that the steam reforming and water gas shift reactions had been almost completely deactivated by the end of the 6th cycle. The catalyst deactivation process was not observed when using waste cooking vegetable oil [8, 9] and suggests fouling via trace elements known to be present in lubricating oil.

Traditional lubricating oil additives include the elements molybdenum, calcium, phosphorus, sulphur, zinc and magnesium, which perform a number of important functions including friction modification, anti-wear, anti-oxidant, detergent and neutralisation of acidity [11].

These additives can be transported into the vehicle exhaust system and cause problems with emissions control catalysts. As a result there have been attempts to replace these elements by more benign species such as those based on boron [12]. Other inorganics are associated with clogging of diesel particulate filters with 'inorganic ash', while in gasoline engines they can be responsible for tailpipe inorganic nanoparticles [13].

Despite each step in the chemical looping reforming process being active and initially very efficient, as shown by the high H_2 yield efficiency, the deactivation of the steam reforming and water gas shift reactions needs to be investigated and resolved before the looping process can be viably sustained. Further optimisation could in all likelihood require removing the lubricating oil ash and additives and minimising the formation of the CH_4 by-product. This would then be followed by coupling the CLR process with in-situ CO_2 sorption, to achieve maximum H_2 yield.

SUMMARY/CONCLUSIONS

The individual reaction steps making up for a potentially successful chemical looping reforming process using waste lubricating oil have been observed using the CLR process, with high H_2 yield in the first cycle.

The CLR process is appropriate for reforming of complex oils such as lubricating oil due to the ability to cyclically eliminate carbonaceous deposits. This occurs simultaneously with Ni oxidation thus supporting the endothermicity of the steam reforming reaction. The waste lubricating oil was also verified to cyclically reduce the NiO.

A loss of catalyst activity was observed over repeated cycles due to deactivation of the steam reforming and the water gas shift reactions, which had an adverse effect on the H_2 yield. The reason for this is under investigation but is likely to be due to catalyst fouling, i.e. from the formation of refractory deposits containing the Mo, P, Ca, S, Zn and Mg lubrication additives.

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DEFINITIONS/ABBREVIATIONS

CLR   : Chemical Looping Reforming

H_2 Yield Eff   : Hydrogen yield efficiency (mol H_2/mol C from fuel)/(theoretical max)

OTM   : Oxygen Transfer Material

TGA   : Thermo-Gravimetric Analysis

R   : Reaction

RWGS: Reverse water gas shift

S   : Selectivity of carbon containing product

T   : Temperature

WHSV: Weight hourly space velocity (mass flow rate of reactants per unit mass of catalyst)

WGS   : Water gas shift

X   : Mass loss conversion fraction

X_{oil} : Conversion fraction of lubricating oil

X_{H2O} : Conversion fraction of water

Table 1: Conversions and products selectivity for 6 cycles of CLR. S:C=2.5, T=600°C.

	Chemical looping reforming experiments					
Cycle	X_{oil}	X_{H2O}	Sel. CO	Sel. CO_2	Sel. CH_4	H_2 yield eff
1	.944	.535	.432	.482	.085	.712
2	.848	.481	.402	.521	.077	.642
3	.900	.319	.473	.466	.062	.528
4	.936	.162	.474	.460	.065	.401
5	.792	.177	.457	.463	.079	.366
6	.782	.097	.418	.509	.073	.301
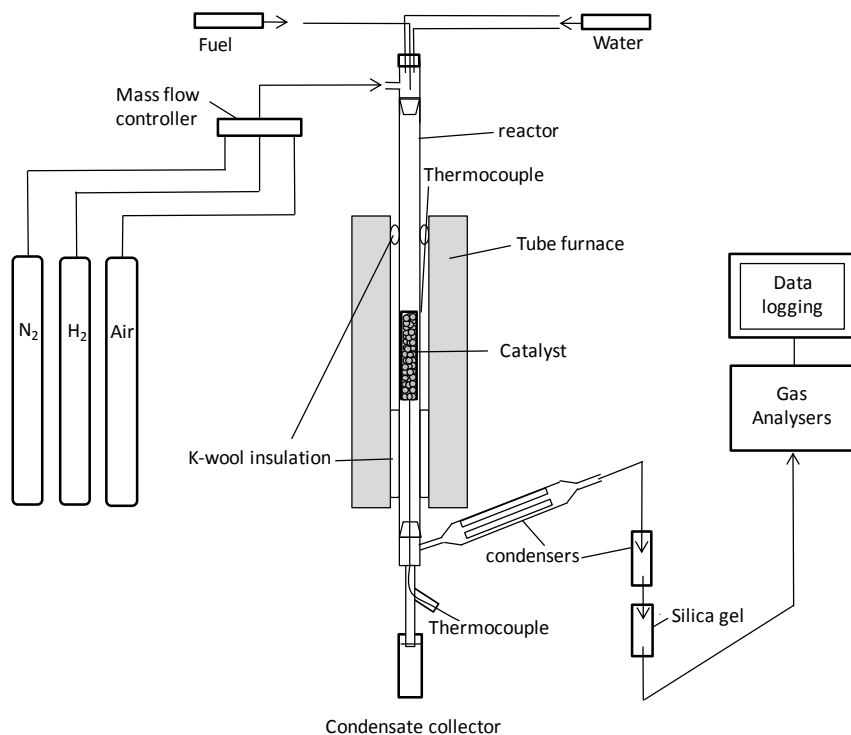
Figure 1: Experimental set-up
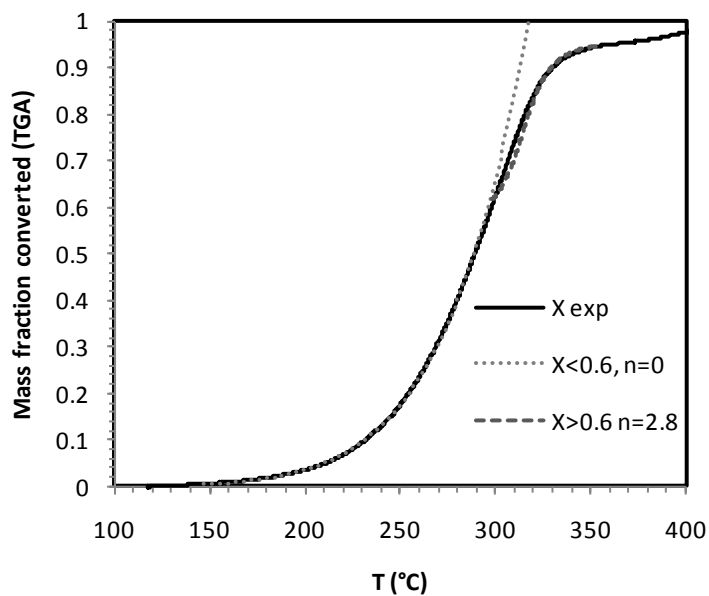
Figure 2: Mass loss conversion fraction (X) vs. temperature (T) in TGA under nitrogen flow and 6 °C/min, experimental fraction, and the modelled mass conversion fractions for the two stages using nth order reaction model: below and above 300 °C, for X below and above 0.6.
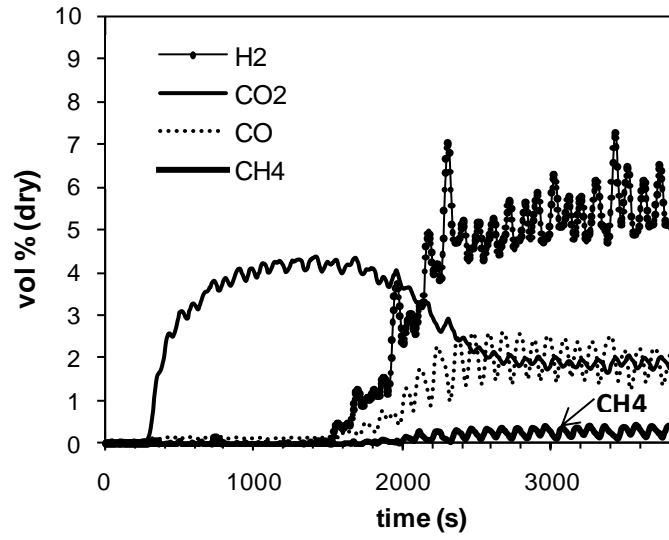
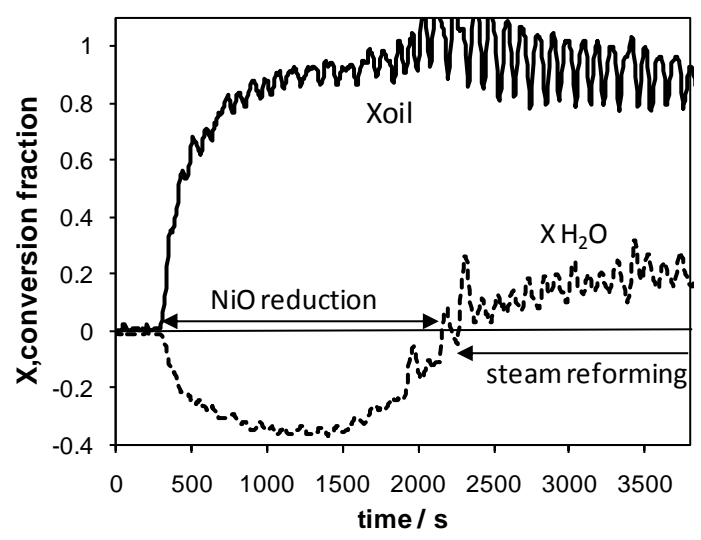Figure 3: Dry reformate analysis from cycle 4, using S:C=2.5, T= 600 ℃

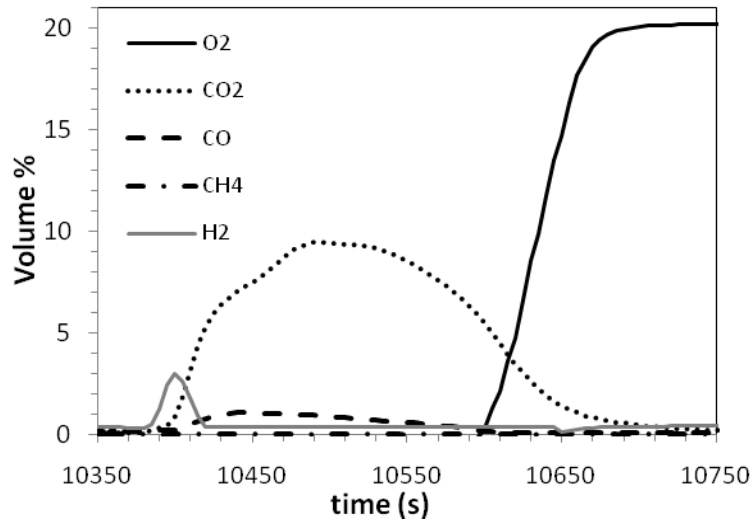Figure 4: Conversion of oil and water during fuel-feed step, cycle 4 using S:C=2.5, T=600 ℃

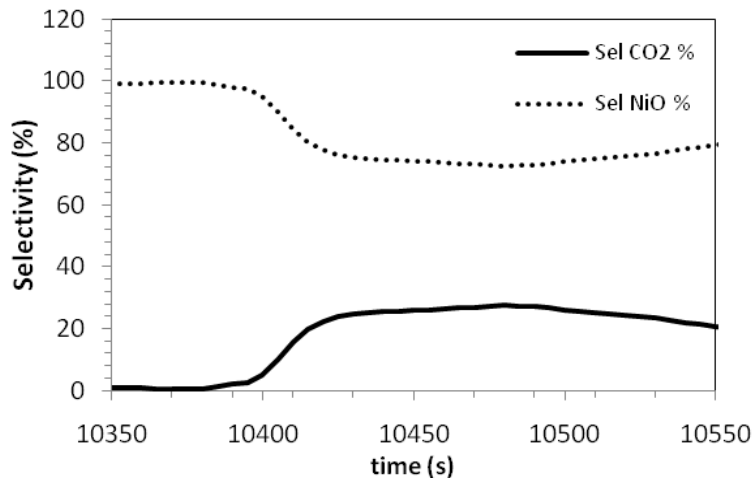Figure 5: Dry gas analysis from cycle 2, using S:C=2.5, T=600ºC

Figure 6: Selectivity of oxygen containing products during oxidation step based on C→CO$_2$
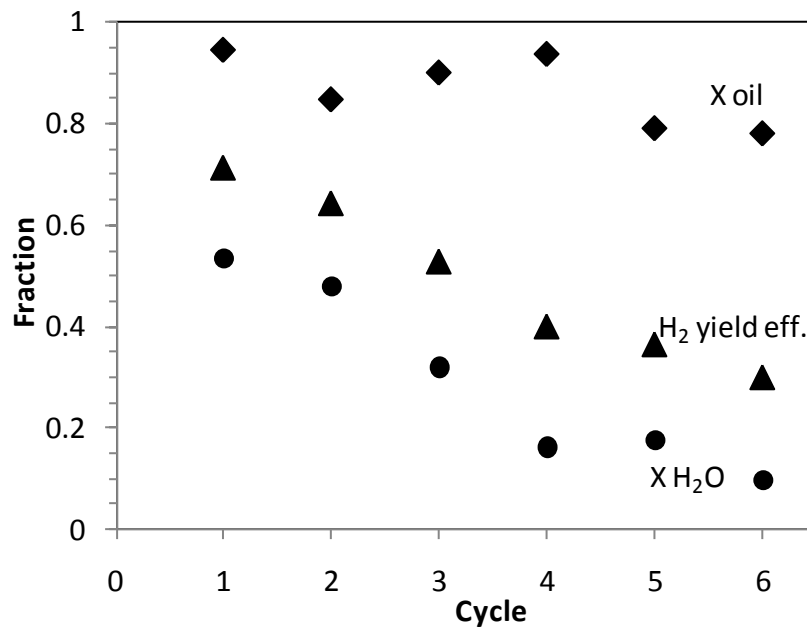rate and Ni→NiO rates.

Figure 7: Comparison of average fuel conversion, water conversion and hydrogen yield efficiency across 6 cycles of CLR. S:C=2.5, T=600 °C.