

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% H₂, 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/ Al₂O₃ catalyst as the oxygen transfer material (OTM). An oil conversion rate based on carbon species (CO, CO₂ and CH₄) of up to ~95% was achieved. The steam to hydrogen conversion of 53%, accounted for 63% of the total H₂ produced, compared to the theoretical ideal of 67.4%. The syngas composition was initially >65 vol% H₂, 15 vol% CO, 15 vol% CO₂, and <5 vol% CH₄. 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 880°C used for the cracking process, the H₂ 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 CO₂-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 Al₂O₃ 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 CH₄, CO and CO₂ were measured using a Uras 14 infrared absorption analyser, H₂ was measured using a Caldos 15 thermal conductivity analyser and O₂ 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 °C 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 H₂ in order to pre-activate the catalyst. After that the cycles comprised of the fuel/water feed using N₂ as a carrier gas, followed by a N₂ purge, completed by an oxidation step using air. Effectively, 6 cycles were equivalent to 12 reactive steps, not counting the potential reactions during the N₂ purge. It should be noted that in full-scale operation of the process, the N₂ 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 H₂ 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 cm³ 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.

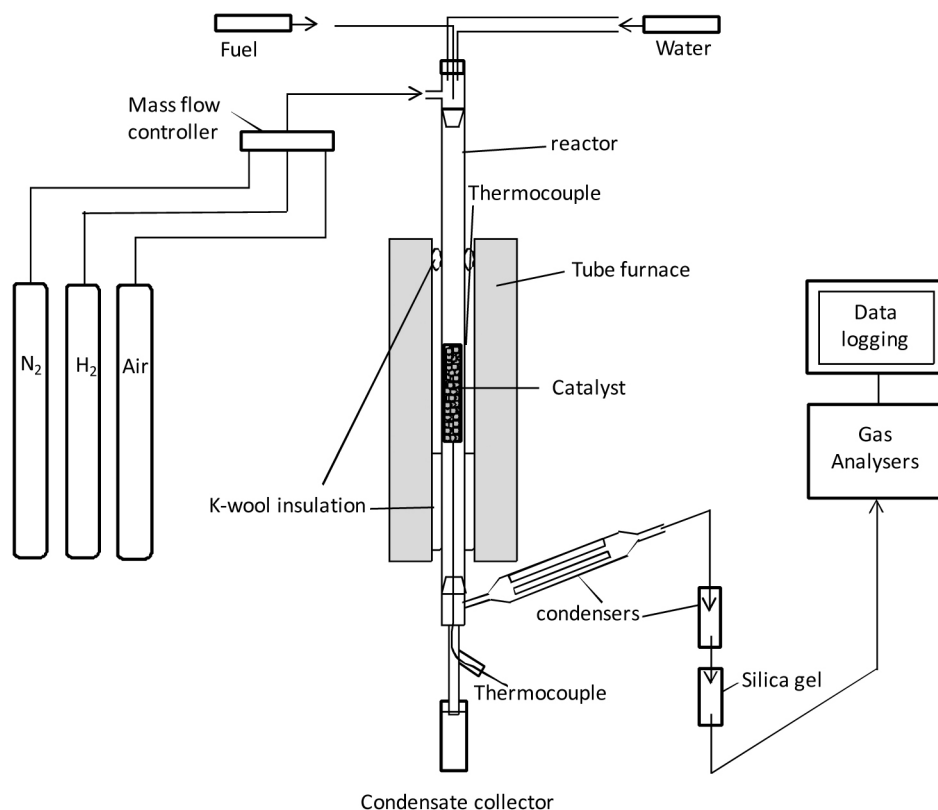
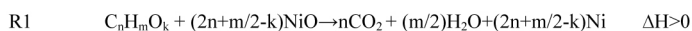


Figure 1. Experimental set-up

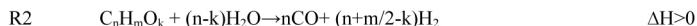
The reactions occurring during the fuel feed step are summarised below:

- Fuel thermal decomposition on NiO bed causes NiO to reduce to Ni (2nd cycle onwards).
- This is done via the reaction of ‘unmixed combustion’:



(This stage produces the most C deposits)

Once Ni sufficiently reduced, steam reforming occurs



And the water gas shift reaction follows.



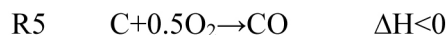
It can be seen that the steam reforming reaction is endothermic and so heat is required to maintain the required temperature. It is worthy to note that though reactions R2 and R3 represent the main H₂ production reactions, the maximum contribution of the steam reactant to the H₂ yield is $(2n-k) / (2n+0.5m-k)$, 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 H₂-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 N₂ 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 N₂ gas was switched off and replaced by a flow of air at 1000 cm³ 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.



Ni oxidation on support

