
Published article:

Dou, B, Rickett, GL, Dupont, V, Williams, PT, Chen, H, Ding, Y and Ghadiri, M (2010) *Steam reforming of crude glycerol with in situ CO(2) sorption.* Bioresource Technology, 101 (7). 2436 - 2442. ISSN 0960-8524

http://dx.doi.org/10.1016/j.biortech.2009.10.092

Steam reforming of crude glycerol with in-situ CO_2 sorption

Binlin Dou, Gavin L. Rickett, Valerie Dupont*, Paul T. Williams, Haisheng Chen,
Yulong Ding, Mojtaba Ghadiri.

School of Process, Environmental and Materials Engineering, University of Leeds,
Leeds, LS2 9JT, UK

Corresponding author: V.Dupont@leeds.ac.uk

Paper accepted and published. Full reference:

Binlin Dou, Gavin L. Rickett, Valerie Dupont, Paul T. Williams, Haisheng Chen, Yulong Ding, Mojtaba Ghadiri. Steam reforming of crude glycerol with in situ CO_2 sorption, Bioresource Technology 101 (2010) 2436–2442.

ABSTRACT

Steam reforming of the crude glycerol by-product of a biodiesel production plant has been evaluated experimentally at atmospheric pressure, with and without in-situ CO_2 sorption, in a continuous flow fixed-bed reactor between 400 and 700 °C. The process outputs were compared to those using pure glycerol. Thermodynamic equilibrium calculations were used to assess the effect on the steam reforming process of the main crude impurities (methanol and four fatty acid methyl esters). The crude glycerol and steam conversions and the H_2 purity reached 100%, 11% and 68% respectively at 600 °C. No CH_4 was found at and above 600 °C. Steam reforming of crude glycerol with *in-situ* CO_2 removal is shown to be an effective means of achieving hydrogen purity above 88% in pre-CO_2 breakthrough conditions.

Keywords: Steam reforming; Crude glycerol; H_2; Catalyst, CO_2-sorbent

---

[*] Author to whom correspondence should be addressed. Tel: 44 -113-3432503; Fax: 44 -113-2467310, v.dupont@leeds.ac.uk.

1. Introduction

Crude glycerol, a by-product of manufacturing biodiesel, has been produced at increasing levels in recent years. It consists of the heavy liquid phase produced as a result of the transesterification of animal fats and vegetable oils, has high impurity content. These include water, methanol, fatty acid methyl esters, and to a lesser extent, unreacted fatty acids, soaps, metals and minerals. Water is often added to the crude at typically ca. 10 % vol. at refineries to decrease its viscosity for ease of handling. The literature thus far shows that crude glycerol composition varies widely (Slinn *et al.*, 2008, Valliyappan *et al.*, 2008, Dou *et al.*, 2009a, Hansen *et al.*, 2009). This makes it a poor quality and unpredictable fuel and currently has little industrial use.

Finding solutions to using crude glycerol economically is seen as vital in lowering the cost of biodiesel manufacture and increasing its commercialization. There have been experimental studies into steam reforming of pure glycerol (Adhikari *et al.*, 2007ab & 2008, Douette *et al.*, 2007, Hirai *et al.*, 2005, Zhang *et al.*, 2007) but little has been published on steam reforming or steam gasification of the crude glycerol by-product of biodiesel (Slinn *et al.*, 2008, Valliyappan *et al.*, 2008). One mol of pure glycerol, which has the chemical formula of $C_3H_5(OH)_{3,}$ can theoretically produce 7 mol of hydrogen and three mol of CO_2, assuming complete conversion through the complete steam reforming reaction. The latter effectively represents the combined effects of thermal decomposition of glycerol followed by water gas shift reaction.

The maximum purity of H_2 in the syngas achievable without sorption enhancement is therefore 70%. Thermodynamic analyses have helped identify the optimum conditions for hydrogen production via steam reforming of glycerol (Adhikari *et al.*, 2007a,c, Chen *et al.*, 2009). Hirai *et al.*, (2005) reported a H_2 selectivity of 90% and complete conversation at 600 ^oC when using a Ru/Y_2O_3 catalyst. The work of Zhang *et al.*, (2007) obtained a 100 % glycerol conversion when steam reforming glycerol over a ceria-supported metal catalyst at only 400 ^oC. Adhikari *et al.*, (2007b) used an alumina supported metal catalyst to perform glycerol steam reforming and found that high temperatures yielded high selectivity of up to the theoretical maximum of 70%. Direct comparisons between pure and crude glycerol steam reforming can be found in Slinn *et al.*, (2008) and Valliyappan *et al.*, (2008). In order to increase the efficiency of steam reforming, a CO_2 sorbent may be added in the reactor bed to remove CO_2 and thereby driving the water gas shift reaction forward, increasing H_2 production, fuel conversion and H_2 purity in the syngas, while decreasing non-CO_2 carbon containing products. To date, this concept applied to methane steam reforming has been the subject of intensive research (Ding and Alpay, 2000, Harrison, 2008). Work by the authors of the present study has shown that a gas stream containing 95% H_2 (dry) can be achieved by using calcined dolomite (CaO) as a sorbent (Dou *et al.*, 2009b) during steam reforming of pure glycerol. The present study aims to achieve similar purity levels with the more challenging crude. An investigation of the thermogravimetric kinetics of the same crude glycerol as was used in the present study is reported in Dou *et al.*, (2009a). The latter showed that the crude glycerol exhibited four phases of decomposition with increasing temperature at a rate of 5 K min^{-1}, which were attributed to the evaporation of water and evaporation/decomposition of methanol below 150 °C, then, mainly thermal decomposition of glycerol up to 230 °C, followed by decomposition products of fatty acid methyl esters and other impurities up to 435 °C and finally tarry residues to up to 850 °C. A detailed study of temperature, pressure, steam to glycerol ratio, fractional

CO_2 sorption and N_2 dilution effects on the thermodynamic equilibrium of steam reforming of pure glycerol with CO_2 sorption was also conducted as part of this project and the results are presented in Chen *et al.,* (2009). The most favourable conditions for sorption enhanced steam reforming of pure glycerol were found to be 800-850 K (527-577 °C), 1 bar, and steam to carbon ratio of 3. CO_2 sorption was found to increase fuel conversion and prevent carbon formation below 900 K. Increasing dilution with N_2 had the effect of increasing H_2 and CO_2 and reducing CH_4 through the reaction's sensitivity to partial pressures. The experimental study presented here is therefore conducted at or around these theoretical optimum conditions.

2. Materials and Methods

2.1 Materials

2.1.1 Crude glycerol

The crude glycerol was obtained from D1-Oils Ltd, Middlesborough, UK. It mainly consisted of 70-90 wt% glycerol, with water as well as methanol contents lower than 15 wt%, based on the data sheet from Directive 2001/58/EC provided by the manufacturer. The content of C, H, N and S in the crude glycerol consisted of 36.21 wt% carbon, 9.07 wt% hydrogen, 0.07 wt% nitrogen and no sulphur, by analysis using a CE Instrument Flash EA 1112 Series. The calculated average elemental molar formula was therefore $C_{3\pm0.2}H_{8.9\pm0.4}O_{3.4\pm0.2}N_{(5\pm2)\times10^{-3}}$ with the O content derived by difference between 1 and the sum of the measured C, H, and N mass fractions. This indicated higher H/C and O/C ratios compared to pure glycerol. The latter would have partly resulted from the presence of water and methanol in the crude. However the fatty acid methyl esters impurities whose H/C and O/C ratios are lower than those of glycerol have the opposite effect. The liquid density of the crude was measured at 1386 kg m^{-3} at 20 °C compared to 1261 kg m^{-3} for pure glycerol. The higher calorific value of the crude was measured using a Parr Autoclave Reactor and the value 20.08 MJ/kg was obtained, which was close to 19 MJ/kg for pure glycerol, reflecting its high glycerol content. Simple, non-quantitative characterisation by GC–MS was carried out in this study using a Trace GC 2000 TOP (Thermo Electron Corp.), with a splitless injector and a mass spectrometer Fisons MD800. The column used for GC was a 25 m×0.25 mm RESTEK RT 5ms and helium at 1 ml min^{-1} flow rate was used as the carrier gas. The GC-MS analysis was performed using an oven programmed to go from 333 to 583 K at a rate of 5 K min^{-1}. The solvent that was used to dissolve the crude glycerol was methanol. The composition of crude glycerol varies depending on the crop or animal oils used as the primary source. The GC-MS spectrum of the sample revealed the presence of the following components: glycerol, linoleic ($C_{19}H_{34}O_2$), palmitic ($C_{17}H_{34}O_2$), oleic ($C_{19}H_{36}O_2$), and stearic ($C_{19}H_{38}O_2$) acid methyl esters. Glycerol of 99.1% purity was obtained from Sigma-Aldrich Inc (G6279) and was subjected to the same experiments for comparisons and detailed results on the sorption enhanced steam reforming of pure glycerol are presented elsewhere (Dou *et al.*, 2009b) and provide a basis for comparison with crude glycerol in the present study.

2.2.2 Reactor bed materials

The catalyst was a commercial Ni-based steam reforming catalyst manufactured by Johnson Matthey. It was in the form of cylindrical pellets with 13.8 mm diameter, 18.4 mm height, perforated with four equidistant holes of 3.8 mm diameter. The catalyst contained approximately 18 wt% NiO supported on an Al_2O_3 substrate. To attempt to minimise mass transfer effects, the catalyst was crushed to a size range of 0.66-1.70 mm for the experiments. The dolomite, crushed and sieved to the same size as the catalyst after calcination, originated from the Warmsworth quarry in Northern England. Its composition was 21.3 wt% MgO, 30.7 wt% CaO, 0.3 wt% SiO_2, 0.27 wt% Fe_2O_3, and 0.1 wt% Al_2O_3. High resolution scanning electron microscopy (SEM) (LEO 1530) coupled to an energy-dispersive X-ray spectrograph (EDXS) were used to study the morphology of the fresh, reduced and used catalyst.

2.2 Experimental setup

The experimental set up has been described in detail in Dou *et al*., (2009b). The system consisted of a continuous flow, fixed-bed, quartz micro reactor vertically placed in a temperature controlled oven. The details of the reactor are shown in Fig. 1. The reactor had an internal diameter (ID) of 0.025 m and was 0.70 m long. An injector supplied 4 ml hr^{-1} of the mixture of glycerol and water in the lower part of the reactor. The liquid glycerol/water mixture with a preset ratio was injected by a programmable syringe pump (New Era Pump Systems Ltd. UK) into the injector. As the injector was housed in the furnace, the mixture was heated above 300 °C vaporising it, and subsequently met with 500 cm^3 min^{-1} (STP) of a diluting N_2 gas stream (MKS mass flow controller). The glycerol/nitrogen mixture was then passed to 5 g of the catalyst or 5 g of the catalyst intimately mixed with 5 g of dolomite when conducting experiments with in-situ CO_2-sorption. Two K-type thermocouples measured the injector outlet temperature and the catalyst bed temperature. The feed gas composition of $C/H_2O/N_2$ for all the reforming experiments was kept at about 0.84/2.59/22.30 molar ratio, achieving a steam to carbon (S/C) ratio of 3.0, using the elemental formula and density of the crude glycerol to achieve the correct flows. The extent of N_2 dilution used here was prompted by the need to achieve a nominal flow of dry gases in the on-line analysers. In the absence of sorbent, the use of the N_2 carrier permits closure of the elemental balance thereby allowing the calculation of reactants conversions and products yield. Experiments were performed at 400, 500, 600 and 700 °C with and without CO_2 sorbent as in Dou *et al.,* (2009b).

Before each experiment, the catalyst was reduced with a continuous flow of 30 cm^3 min^{-1} H_2 mixed with 500 cm^3 min^{-1} N_2 (STP) at 400 °C for 2 hours. The dolomite was calcined at 900 °C for at least 4 hours to obtain the desired oxidised form before being weighed and loaded in the reactor. Previous studies indicated that once calcined, the MgO in the dolomite is no longer able to carbonate and only the CaO component remains active as a CO_2 sorbent (Bandi *et al.*, 2002, Dupont *et al.*, 2008).

2.3 Products analysis

A set of three (Caldos, Magnos and Uras) online analysers from ABB, Advanced Optima series, were used to record every 5 seconds the main gas concentrations in the reactor effluents. The Caldos 15 measured the concentration of H_2 using a thermal conductivity detector, the Magnos 106 recorded the concentration of O_2 be means of a paramagnetic cell and the Uras 14 analyser measured CO, CO_2 and CH_4 concentration by infra-red absorption. In addition, gaseous products were collected in a 5 L Tedlar™ sample bag and were analysed by two separate gas chromatographs. Hydrocarbons from C_1 to C_4 such as CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10} were determined using a Varian 3380 gas chromatograph with a flame ionisation detector (GC/FID). Nitrogen was used as the carrier gas with a 2 m×2 mm column packed with 80-100 mesh Haysep packing material. The oven temperature was set at 60 °C for 3 min, then programmed to 100 °C at a heating rate of 5 °C min^{-1}, and held for 3 min, finally heated to 120 °C at a heating rate of 20 °C min^{-1} and held for 17 min at the final temperature. Permanent gases (H_2, CO, O_2, N_2 and CO_2) were analysed by a second Varian 3380 GC with two packed columns and with two thermal conductivity detectors (GC/TCD). Hydrogen, oxygen and carbon monoxide and nitrogen were analysed on a 2 m × 2 mm column, packed with 60-80 mesh molecular sieve. Argon was used as the carrier gas. Carbon dioxide was analysed on a 2 m × 2 mm column with Haysep 80-100 mesh packing material. The gas chromatograph oven was held isothermally at 40 ºC for the analysis. The detector oven was operated at 120 ºC with filament temperature at 160ºC (Wu and Williams, 2008). The sporadic off-line analyses were used as means of verifying the accuracy of the online analysers with respect to the mol fractions of species CO, CO_2, H_2 and CH_4, and provided means of obtaining an independent value for N_2 (normally inferred every 5 s by difference from 1 of the sum of the online mol fractions of H_2, CO, CO_2, CH_4). In addition they provided confirmation that there were no higher hydrocarbons products.

2.4. Formulae for the data analyses

The conversion calculation of crude glycerol is based on a carbon balance between the inlet and the outlet of the reactor:

$$x_{gly}(\%) = \frac{\dot{n}_{dry,out}\sum y_{c,out}}{\dot{n}_{C,in}} \times 100 \qquad (1)$$

where '$\dot{n}$'and 'y' are relevant molar flow rates (mol s^{-1}) and gas mol fractions respectively, the subscript '*c,out*' indicating all measured carbon-containing gas products and $\dot{n}_{dry,out}$ is the dry total molar flow of gases leaving the reactor calculated through an elemental balance of nitrogen:

$$\dot{n}_{dry,out} = \frac{\dot{n}_{N2,in}}{y_{N2,out}} = \frac{\dot{n}_{N2,in}}{\left(1 - \sum_{\text{dry gases,out}} \mathrm{y_i}\right)} = \frac{\dot{n}_{N2,in}}{\left(1 - \left(y_{H2} + y_{CO2} + y_{CO} + y_{CH4}\right)\right)} \qquad (2)$$

The conversion of steam derived from measurements is given by:

$$x_{H2O}(\%) = \frac{\dot{n}_{H2O,in} - \dot{n}_{H2O,out}}{\dot{n}_{H2O,in}} \times 100 = \frac{\dot{n}_{dry,out}\left(y_{H2} + 2y_{CH4}\right) - \beta x_{gly}\dot{n}_{gly,in}}{\dot{n}_{H2O,in}} \qquad (3)$$

which is based on the hydrogen elemental balance, whereby the molar outflow of hydrogen products (on 2H basis) is β times that of converted fuel (β is 4 for pure glycerol and 4.45 for the crude glycerol, from elemental analysis) added to the converted molar flow of steam.

The syngas composition is reported as dry gas concentrations of gases, sometimes corrected for zero N_2 diluent content, e.g. for hydrogen, it is the ratio of H_2 volume fraction to the sum of the volume fractions of H_2, CO, CO_2 and CH_4 at the outlet, and is also termed 'H_2 purity'. For the steam reforming reaction of any oxygenated hydrocarbon $C_nH_mO_k$, the maximum H_2 purity achievable in theory in the absence of CO_2 sorbent and not counting thermodynamic equilibrium effects is:

$$\%\max \mathrm{H_2\ purity} = 100 \times \frac{{}^{m}\!/_{2} + 2n - k}{{}^{m}\!/_{2} + 3n - k} \qquad (4)$$

For instance, for pure glycerol ($n = 3$, $m = 8$, $k = 3$) it is 70%, whereas for methanol ($n = 1$, $m = 4$, $k = 1$) it is 75%. Using the crude's elemental formula ($n = 3$, $m = 8.9$, $k = 3.4$) a maximum theoretical H_2 purity of 70.15% is found. In the experiments with the CO_2 sorbent, the glycerol conversion cannot be calculated on the basis of equations (1) and (2). This is because the carbon products include the solid carbonate and the latter's rate of sorption is not quantifiable experimentally as a time-dependent parameter in the described setup. Therefore, the experimental results with the CO_2-sorbent do not report glycerol or steam conversions, but are presented in terms of H_2 purity and syngas composition as in Dou *et al.*, (2009b).

2.5 Thermodynamic equilibrium calculations

Following the same method reported in Dou *et al.*, (2009b), the code EQUIL from the CHEMKIN package (Kee et al., 1980) was used to estimate the effects of some of the crude glycerol's major impurities on the reactants conversions and products selectivity on the steam reforming process at thermodynamic equilibrium. This was calculated in the absence of CO_2 sorbent in the temperature range of the experiments (400-700 °C) using 10 °C increments. The equilibrium of steam reforming of methanol, and the methyl esters of oleic, linoleic, stearic and palmitic acid were also calculated. The thermodynamic properties of methanol are well-known. In contrast, the specific heat, enthalpy and entropy polynomials of temperature of the four methyl esters, required as inputs to the program, were fitted from the data reported in Osmont *et al.*, (2007), which were derived from quantum chemistry theory using the anharmonic oscillator approximation.

3. Results and discussion

3.1 Fuel and steam conversions: comparison of pure and crude glycerol without CO_2 sorbent

Importance was given to the steam conversion in addition to the fuel conversion as a true reflection of steam reforming activity, since glycerol can thermally decompose yielding H_2 product in absence of catalyst, albeit generating many oxygenated hydrocarbons (Dou *et al.*, 2009a). These steam and fuel fractional conversions obtained for pure glycerol are reproduced in Figure 2, alongside the new experimental outputs on crude glycerol and the equilibrium calculations on methanol and the four fatty acid methyl esters investigated. Comparison of the online measurements with their off-line GC analysis counterparts showed that they was an average relative error of 5% between them. It is worth noting that the FAMEs yielded equilibrium values extremely close to each other and therefore only the outputs for palmitic acid methyl ester steam reforming, are shown in Fig. 2 as the representative of the four FAMEs investigated. Figure 2 indicates that the crude glycerol conversions were 71, 96, 100% at 400, 500, 600 °C respectively, surprisingly exceeding only by a few percent those of the pure glycerol under the same reaction conditions (63, 92, 97%). Equilibrium calculations of glycerol, methanol, palmitic-, stearic-, oleic- and linoleic- acid methyl esters with a steam to carbon ratio of 3 with the same N_2 dilution as in the experiments yielded fuel conversions of 100% for all the fuels and the whole temperature range. Therefore pure and crude glycerol conversions achieve near their equilibrium optimum between 500 and 700 °C. Coke deposition over the catalyst was shown to have taken place using SEM imaging of the catalyst following the 400 °C steam reforming experiment of the crude glycerol. Significant carbon deposition was an effect of the incomplete fuel conversion observed at this temperature. This is in agreement with the TGA experiments on the crude glycerol, which yielded larger carbonaceous residues than the pure glycerol.

At and above 500 °C, the largest discrepancy between crude and pure glycerol was found in the steam conversions. Whereas those of pure glycerol were ca 23% between

500 and 700 °C, i.e. near their predicted thermodynamics equilibrium optimum, those of the crude glycerol were much lower at around 11%. Since the equilibrium steam conversions of the impurities methanol and FAMEs were significantly higher than those of pure glycerol at any given temperature, the lower crude glycerol steam conversions were not due to the individual steam reforming contributions of the main crude impurities. The presence of thermally resistant residues from the thermal decomposition of the crude glycerol mixture components in the preheating zone could account for the steam conversions being further from equilibrium than those found obtained for pure glycerol, (11% as opposed to the expected mid-20%s). Increasing the residence time in the reactor may therefore improve the steam conversion for the current set of conditions. Without affecting the yield of hydrogen, this may be achieved using a lower N_2 flow than in the experiments reported here, although in the present experimental set up, although this would bring the analysers near to the minimum sample gas flow required for their good operation.

3.2. Products distribution: comparison of pure-crude glycerol without CO_2 sorbent

GC analysis revealed there was no significant production of the hydrocarbon products C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10} at the temperatures investigated. The main gaseous products were therefore H_2, CO_2, CO and CH_4, confirming the validity of equations (2) and (3) and were used to calculate fuel and steam conversions from experiments for those temperatures where carbon deposition was negligible (at and above 500 °C). Previous work by other research groups also indicates that above temperatures of 400 °C, H_2, CO_2, CH_4 and CO have been shown to be the only products (Douette *et al.*, 2007, Adhikari *et al.*, 2007b, Hirai *et al.*, 2005, Zhang *et al.*, 2007).

The effect of temperature on dry gas product composition corrected for zero N_2 is shown in Fig. 3. For each measured species (H_2, CO_2, CO, CH_4) from the pure and the crude glycerol steam reforming, the equivalent equilibrium values are also shown for glycerol (‘gly’) and the crude impurities (methanol ‘mnol’ and the four FAMEs in the shape of palmitic-AME ‘pame’) as in Fig. 2. The largest discrepancies compared with equilibrium model values could be observed at 400 °C, as was the case for the pure glycerol, which corresponded to a low experimental fuel conversion and significant carbon deposition. At 400 °C, the equilibrium calculations predicted significant CH_4 (between 15 and 20%) but the measured amounts were between 5 and 10%, with no other alkanes or alkenes present. This was explained by the presence of the solid carbon in the experiments that would not have been taken into account by the present equilibrium predictions. At and above 500 °C, small differences between the pure and crude glycerol could be seen. CO from the crude was lower by a few percent, and CO_2 higher by a few percent over the whole 400-700 °C range. Once again, this could not be attributed to the individual steam reforming contributions of the impurities, methanol and FAMEs. Indeed their effect would have been to lower the CO_2 and increase the CO, according to the equilibrium results shown in Fig. 3. However the higher crude glycerol CO_2 to CO ratio than that obtained for pure glycerol may be explained by the combined effects of the TGA experiments’ observations of a faster thermal decomposition yielding increased carbonaceous residues at around 600 °C. This would have generated a volatile thermal decomposition product with overall reduced carbon that would have undergone steam reforming. The resulting higher O/C ratio of this volatile product would have resulted in slightly higher CO_2/CO than that of the pure glycerol, which in contrast, left no carbon residue upon thermal decomposition. The H_2 purity of the pure and the crude glycerol were very close to each other, with the crude exceeding that of the pure glycerol by a few percent (67-68% compared to 65-66%). In terms of H_2 purity, the effects of methanol and FAMEs steam reforming were expected to increase the H_2 purity from the crude steam reforming compared to that of the pure glycerol. Indeed, as mentioned earlier, equation (4) yields a maximum theoretical H_2 purity (ignoring equilibrium effects) of 75% for methanol and 74.2% for palmitic acid methyl ester ($C_{17}H_{34}O_2$), compared to the lower 70% for pure glycerol. The equilibrium calculations of H_2 purity for the steam reforming of glycerol, methanol and palmitic-AME at thermodynamic equilibrium shown in Fig. 3 reflect this order.

The general trends of CO increasing and CO_2 decreasing with temperatures were, as expected, reproduced by the thermodynamic equilibrium calculations and are explained by the reverse water gas shift reaction becoming more favourable at higher temperatures. The CH_4 from the crude was, at and above 500 °C, very close to that of the pure glycerol, and followed closely the equilibrium values for pure glycerol. These showed a decreasing trend with increasing temperatures, with close to zero methane concentrations measured at 600 and 700 °C. This could be attributed to methane steam reforming.

The potential for comparisons of the results obtained here with those of other studies on crude glycerol (Slinn *et al.*, 2008, Valliyappan *et al.*, 2008) is limited because their temperatures were significantly higher (880 and 800 °C respectively) and the nature of their crude was markedly different. The present study however corroborates that steam reforming of crude glycerol is achievable in practice. However, process performance, be it in the form of a lower product yield (Slinn *et al.*, 2008), an increase in char and C2+ by-products (Valliyappan *et al.*, 2008), or a lower steam conversion (present study), is slightly lower than for the pure glycerol in the same conditions.

3.3 Effect of in-situ CO_2 removal on crude glycerol products and H_2 purity

Typical dry gas product distributions for crude glycerol steam reforming with *in-situ* CO_2 removal at 500 °C, 600 °C and 700 °C are shown in Fig. 4 for the first 15 minutes of reaction for the sake of clarity of profiles, although each experiment lasted at least 50 minutes. The results obtained here show that the CO_2 concentrations could be maintained at around 0 vol% with very little CO and CH_4 at 500 °C and 600 °C in the presence of the calcined dolomite sorbent. Our previous thermodynamic equilibrium study on sorption enhanced steam reforming of pure glycerol (Chen *et al.*, 2009) had shown that fuel and steam conversion increases as a result of CO_2 removal. Therefore we can expect that, as the crude conversions were, in the absence of sorbent, 96 and 100% for 500 and 600 °C respectively, these would increase in the presence of the calcined dolomite to close to 100% for both temperatures. The lower CO content was also in agreement with the effects of CO_2 sorption predicted in Chen *et al.*, (2009) for this steam to carbon ratio and temperature range. The CO_2 breakthrough times were longer for the crude than for the pure glycerol at 500 and 600 °C, the larger difference being at 600 °C, with 28 minutes compared to 7 minutes respectively. Results at 700 °C (Fig. 4c) indicated that CO_2 sorption was no longer efficient at this temperature. This was to be expected, as the results for pure glycerol also showed that CO_2 reached its post-breakthrough value by just 5 minutes of operation (Dou *et al.*, 2009b). The hydrogen purity (mol fraction of H_2/sum of mol fractions of H_2, CO, CO_2 and CH_4) as a function of time is shown in Fig. 5 for the crude glycerol with in-situ CO_2 sorption. The maximum H_2 purity was, as expected, obtained in the initial reaction period. The time on stream producing a hydrogen purity of more than 90% exceeded 10 minutes for the temperatures of 500 °C and 600 °C under the experimental conditions, compared to 5 minutes for pure glycerol (Dou *et al*., 2009b). At 700 °C, the maximum H_2 purity was only 80% for a very short time and then it decreased slightly to below 70% at 10 minutes reaction time, which was accompanied by a poor effect for CO_2 removal at this temperature. This is explained by the process conditions reaching temperatures where carbonate decomposition (calcinations) occurs in the presence of steam. Table 1 compiles the dry gas concentrations, H_2 purity, fuel and steam conversions without and with sorbent (in-situ CO_2 capture) for the crude glycerol steam reforming at 500, 600 and 700 °C. The values obtained with CO_2 capture were averages of the first 15 minutes. The largest differences between without and with sorbent can be seen in the CO_2 and CO mol %, and the H_2 purity. The slightly higher CH_4 obtained may reflect that due to an increased fuel conversion, carbon deposits are no longer formed and instead the fuel converted to CH_4, an effect of the pre-equilibrium conditions. This would have been remedied with a longer reaction time. A study by Pimenidou *et al*., (2009) on the kinetics of dolomite carbonation in conditions simulating those of steam reforming has shown that the presence of steam had a great effect on the kinetics of the carbonation, with the result that CO_2 capacities in dry conditions may double in the presence of steam, bringing them to the theoretical maximum. This may explain in part why the crude glycerol experiments with in-situ CO_2 sorption yielded longer breakthrough times than the pure glycerol in the same conditions, as steam conversion were around half those of the pure glycerol experiments, resulting in significantly higher steam partial pressure in the reactor. Other factors may have been at work, involving the interactions of the different reactive environment with the dolomite material, allowing getting closer to the theoretical maximum CO_2 capacity of the sorbent. A better knowledge of

CO_2-sorbents cyclic use in conditions of steam reforming, as well as of the crude composition would be required in order for sorption enhanced steam reforming of crude glycerol to realise its full potential.

4. Conclusions

Crude glycerol steam reforming has been experimentally investigated in a fixed bed reactor over a Ni-based catalyst at 400-700 ^{o}C with and without in-situ CO_2 removal by carbonation of calcined dolomite. The results were compared to those of pure glycerol under the same conditions based on a previous study. Without CO_2 sorbent, fuel conversion and H_2 purity were close to equilibrium calculations between 500 and 700 °C, but the steam conversion was half of that of the pure glycerol. In-situ CO_2 removal with crude glycerol steam reforming produced H_2 purities close to 90% for an extended period of time.

Acknowledgements

The Engineering and Physical Sciences Research Council, UK, is gratefully acknowledged for funding of work through grant EP/F027389/1. Our thanks also go to Mr. Chunfei Wu for GC and SEM analysis; Dr Martyn V. Twigg, Johnson Matthey for providing the steam reforming catalyst, and Mr James Wylie, WBB Minerals, for the (Warmsworth quarry) dolomite.

References

Adhikari, S., Fernando, S., Haryanto, A., 2007a. A Comparative Thermodynamic and Experimental Analysis on Hydrogen Production by Steam Reforming of Glycerin. Energy & Fuels 21(4), 2306–2310.

Adhikari, S., Fernando, S., Haryanto, A., 2007b. Production of hydrogen by steam reforming of glycerine over alumina-supported metal catalysts. Catalysis Today 129(3-4), 355–364.

Adhikari, S., Fernando, S., To, S.D.F., Bricka, R.M., Steele, P.H., Haryanto, A., 2008. Conversion of Glycerol to Hydrogen via a Steam Reforming Process over Nickel Catalysts. Energy & Fuels 22, 1220-1226.

Bandi, A., Specht, M., Sichler, P., Nicoloso, N., 2002. In Situ Gas Conditioning on Fuel Reforming for Hydrogen Generation. Proceedings of the 5th International Symposium on Gas Cleaning, Pittsburgh, PA, Sept.2002.

Chen, H.S., Zhang,T., Dou, B., Dupont, V. , Williams, P.T., Ghadiri, M., and Ding, Y., 2009. Thermodynamic Analyses of Adsorption Enhanced Steam Reforming of Glycerol for Hydrogen Production. International Journal of Hydrogen Energy 34,7208-7222

Ding, Y., Alpay, E., 2000. Adsorption-enhanced steam methane reforming. Chemical Engineering Science 55(18), 3929-3940.

Dou, B., Dupont, V., Williams, P.T., Chen, H.S., Ding, Y., 2009a Thermogravimetric kinetics of crude glycerol. Bioresource Technology, 100 (9), 2613-2620.

Dou, B., Dupont, V., Rickett, G., Blakeman, N., Williams, P.T., Chen, H., Ding, Y., Ghadiri, M., 2009b. Hydrogen Production by Sorption-Enhanced Steam Reforming of Glycerol. Bioresource Technology 100, 3540-3547.

Douette, A.M.D., Turn, S.Q., Wang, W., Keffer, V.I., 2007. Experimental Investigation of Hydrogen Production from Glycerin Reforming. Energy & Fuels 21(6), 3499-3504.

Dupont, V., Ross, A.B., Knight E., Hanley I., Twigg M.V., 2008. Production of hydrogen by unmixed steam reforming of methane. Chemical Engineering Science 63: 2966-2979.

Hansen, C. F., Hernandez, A., Mullan, B. P., Moore, K, Trezona-Murray, M., King, R. H., Pluske, J. R., 2009. Chemical analysis of samples of crude glycerol from the production of biodiesel in Australia, and the effects of feeding crude glycerol to growing-finishing pigs on performance, plasma metabolites and meat quality at slaughter. Animal Production Science, 49(2):154-161.

Harrison, D.P., 2008. Sorption-enhanced hydrogen production: A review. Industrial & Engineering Chemistry Research 47, 6486-6501.

Hirai, T., Ikenaga, N.O., Miyake, T., Suzuki, T., 2005. Production of Hydrogen by Steam Reforming of Glycerin on Ruthenium Catalyst. Energy & Fuels 19, 1761-1762.

Kee, R.J., Miller, J.A., Jefferson, T.H., 1980. CHEMKIN: a general purpose problem-independent, transportable, FORTRAN Chemical Kinetics Code Package. Sandia National Laboratories. Report SAND80-8003.

Osmont, A., Catoire, L., Gokalp, I., 2007. Thermochemistry of Methyl and Ethyl Esters fromVegetable Oils. International Journal of Chemical Kinetics 39(9), 481-491.

Pimenidou, P., Rickett, G.L., Dupont, V. 2009. In-situ CO_2 capture for unmixed steam reforming. Book of extended abstracts of the 8th World Congress of Chemical Engineering (WCCE8), August 23-27 2009, Montreal, Canada.

Slinn, M., Kendall, K., Mallon, K., Andrews, J., 2008. Steam reforming of biodiesel by-product to make renewable hydrogen. Bioresource Technology 99:5851-5858

Valliyappan, T., Ferdous, D., Bakshi, N.N, Dalai, A., K., 2008. Production of Hydrogen and Syngas via Steam Gasification of Glycerol in a Fixed-Bed Reactor. Topics in Catalysis, 49:59-67

Wu, C.F. and Williams, P. T., 2008. Effects of Gasification Temperature and Catalyst Ratio on Hydrogen Production from Catalytic Steam Pyrolysis-Gasification of Polypropylene. Energy & Fuels 22 (6), 4125–4132.

Zhang, B., Tang, X., Li, Y., Xu, Y., Shen, W., 2007. Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. International Journal of Hydrogen Energy 32(13), 2367-2373

Table 1 Summary of results for Crude glycerol steam reforming without and with CO_2 sorption (average of first 15 minutes, pre-CO_2 breakthrough).

T (°C)	Expt/sorbent	Mol % in dry gas				% Purity	% Conversions	
		H_2	CO_2	CH_4	CO	H_2	Crude glycerol	Steam
500	without	5.9	2.4	0.2	0.7	64.1	96	13
500	with	5.07	0.04	0.4	0.24	88.2	>96	>13
600	Without	6.7	2.4	0.1	1.1	65.0	100	14
600	With	5.51	0.2	0.32	0.34	86.5	100	>14
700	Without	6.6	2.1	0	1.2	66.7	97	16
700	With	6.88	1.61	0.06	0.85	73.2	>97	>16

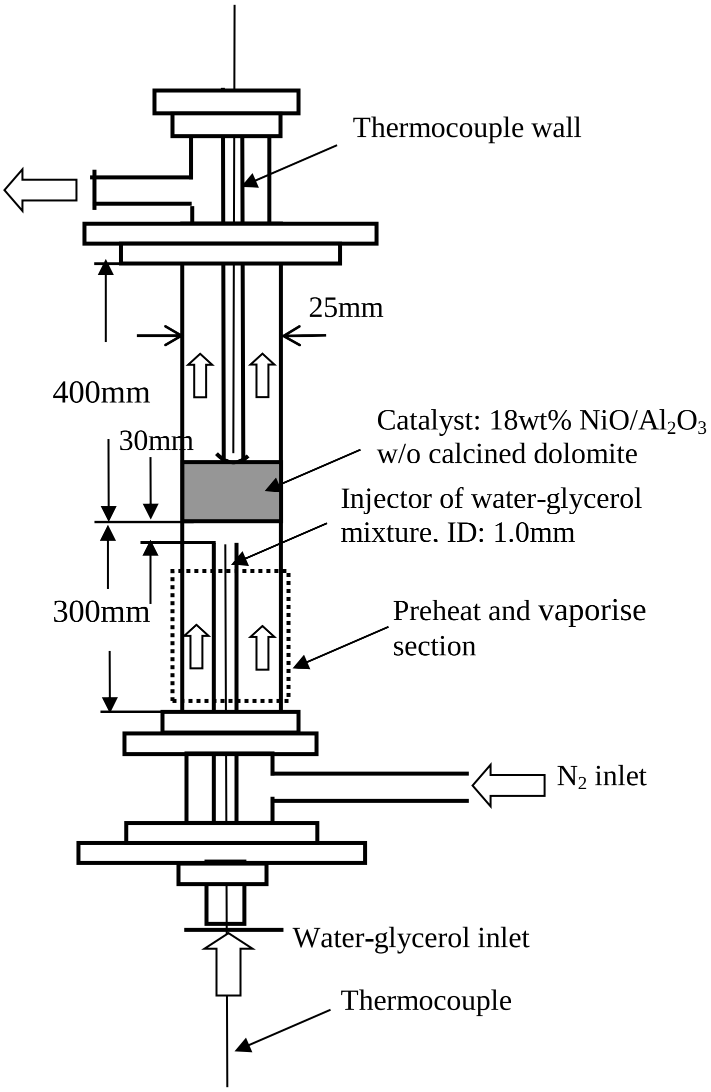


Fig. 1

Fig. 1 Schematic diagram of the reactor.

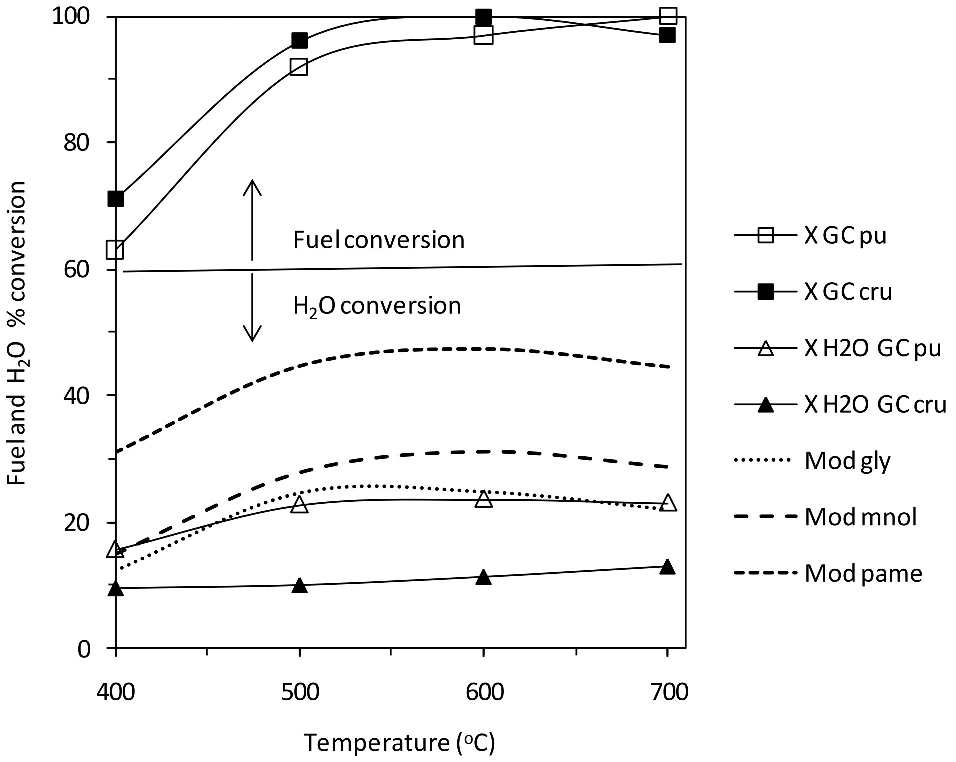


Fig. 2

Fig. 2 Conversions of fuel ‘X’ (graph portion >60%) and of steam ‘X H2O’ (portion below 60%) derived from measurements by gas chromatography ‘GC’ and using thermodynamics equilibrium modelling ‘Mod’ for a Steam:C ratio of 3, using the same N_2 dilution as in the experiments. The following are shown: experimental results for pure ‘pu’ and crude ‘cru’ glycerol , modelling results for glycerol ‘gly’, methanol ‘mnol’ and palmitic acid methyl ester ‘pame’ as a representative of the four FAMEs tested.

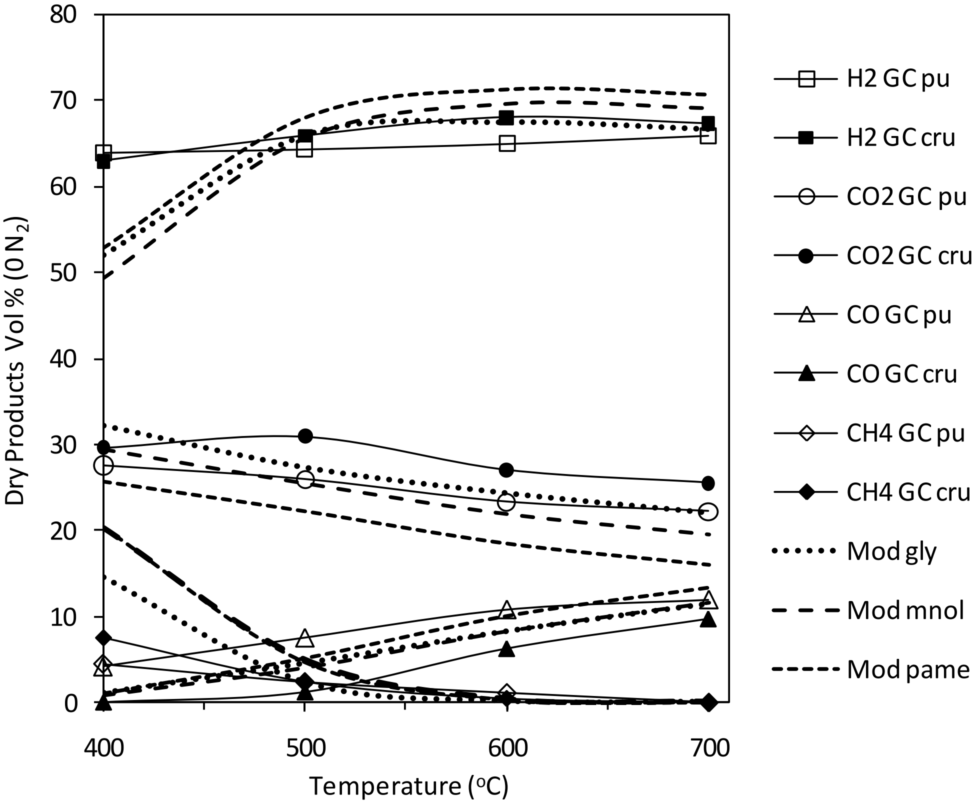
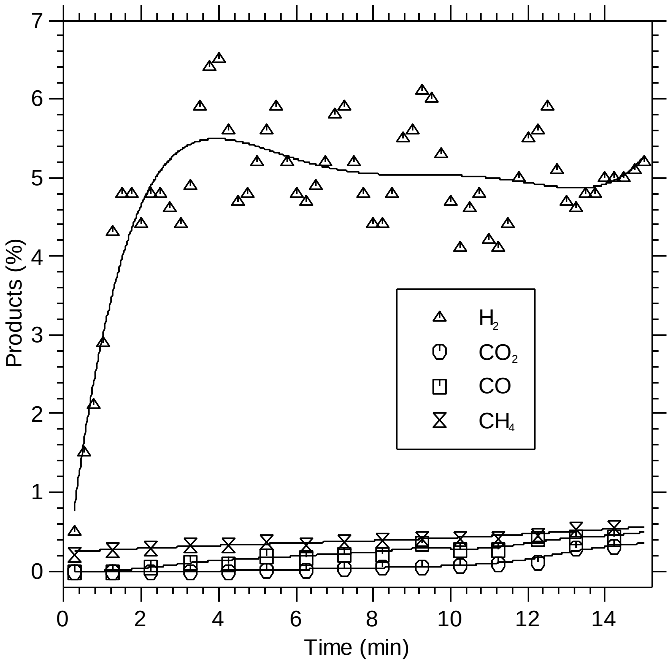


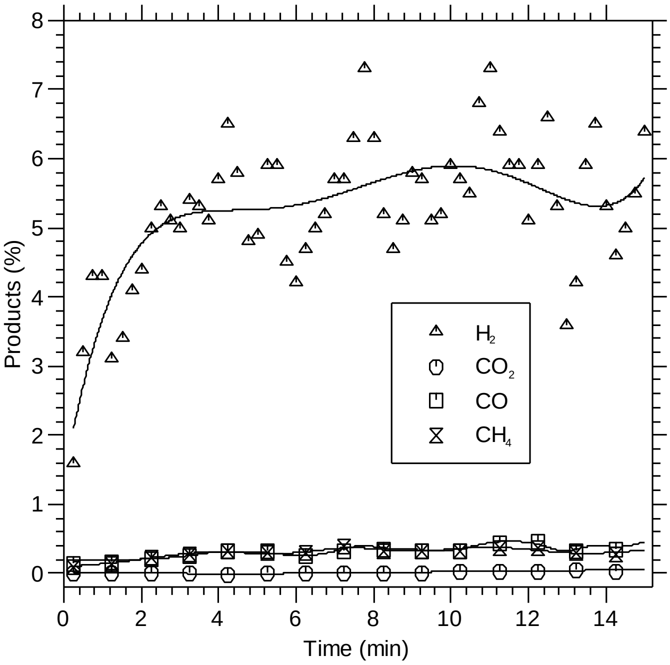
Fig. 3

Fig. 3 Concentrations measured off-line by gas chromatography (GC) and using thermodynamics equilibrium modelling (Mod) for H_2 (H_2 purity), CO_2, CO and CH_4, on a dry basis and corrected for zero N_2, for the same conditions as in Fig. 2.



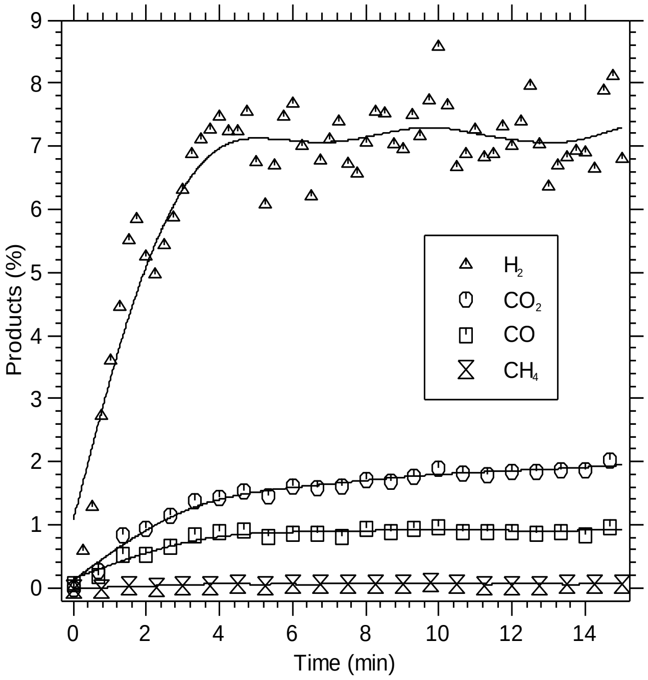
Products (%)
Time (min)
0
1
2
3
4
5
6
7
0
2
4
6
8
10
12
14
H_2
CO_2
CO
CH_4

(a)



Products (%)
Time (min)
0
1
2
3
4
5
6
7
8
0
2
4
6
8
10
12
14
H_2
CO_2
CO
CH_4

(b)



(c)

Fig. 4

Fig. 4 Dry gas concentration of H_2, CO_2, CO and CH_4 products with time from crude glycerol steam reforming with in-situ CO_2 removal, (a), 500 °C; (b), 600 °C; (c), 700 °C. The balance to 100% is N_2.

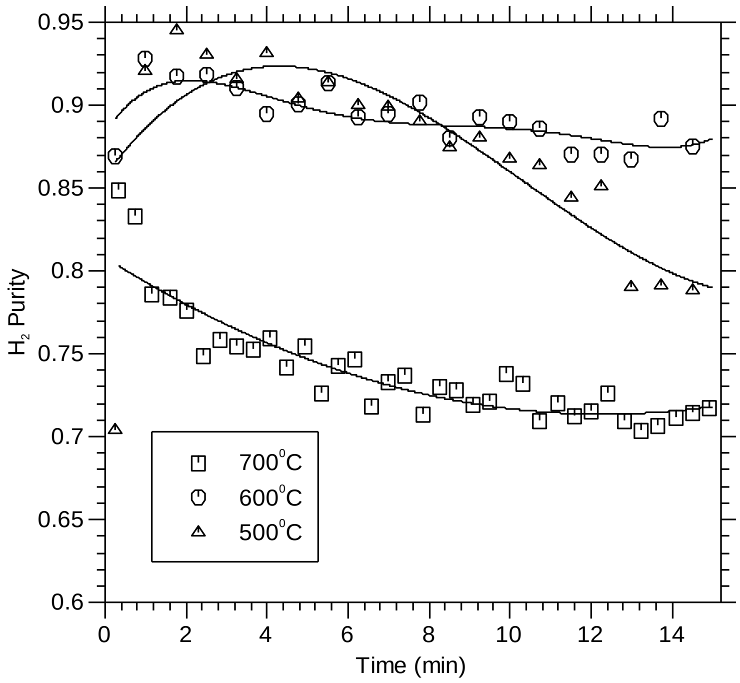


Fig. 5

Fig. 5 H_2 purity (mol H_2 / mol(H_2+CO+CO_2+CH_4) with time for crude glycerol with in-situ CO_2 removal at 500 °C, 600 °C and 700 °C.