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Cold plasma catalysis as a novel approach for valorisation of untreated waste glycerol

Jonathan Harris, Anh N. Phan† and Kui Zhang

Glycerol, a by-product from biodiesel production, is currently considered as waste for disposal. Several attempts have been made to convert this wasted resource for high-value added products via either chemical or biological processes. However, complex steps are required to remove impurities and the selectivity of desired product(s) is low. In this paper, cold plasma catalysis was for the first time proposed to valorise untreated waste glycerol, greatly reducing the negative environmental impacts of waste glycerol. The attractiveness of this approach is that the process can be easily tuned toward specific products with high yields with a very short reaction time (around 16 seconds) at near ambient conditions. By altering the carrier gas, cold plasma power and packing material/catalyst, up to 99% of untreated waste glycerol was converted into either gas products consisting of hydrogen (55 mol% or 7.02 wt%), hydrocarbons (C1-C4: 9-10 wt%), CO (19 wt%) and CO2 (16 wt%), or high value liquid products such as acetol (up to 54 wt%). The findings of this work could open up new opportunities for intensification of green chemical processes and biorefining of waste materials by reducing pre-treatment steps, solvent requirements and amount of waste generation.

Introduction

Depleting fossil fuels reserves, environmental concerns and a highly industrialised society make sustainable clean fuels highly desirable. Bio-fuels (biodiesel from vegetable oils and bioethanol from sugar cane, sugar beets etc.) has been increased yearly to meet individual national targets, i.e 10% renewable energy target for transport sector by 2020 set by the European Union. With the increase in biodiesel production, large amounts of by-product glycerol have been produced, approximately 2.5-3 million tonnes of by-product glycerol are generated annually worldwide.

The by-product glycerol which varies in purity (ranging from 30-85 wt% purity depending on the feedstock and biodiesel production conditions) is currently considered as waste to be discharged. The remainder of the waste glycerol is comprised of impurities such as methanol, alkaline hydroxide catalyst,

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free fatty acids (FFA), soap and water. Therefore, complex purification and separation processing are necessary for pharmaceutical and cosmetic applications. On the other hand, the large surplus of by-product glycerol led to market saturation, causing more than 50% reductions in the value of pure glycerol globally,\(^8\) which makes the purification of by-product waste glycerol uneconomical, particularly for small and medium scaled plants.\(^7,\)\(^9\)

Energy recovery via combustion of waste glycerol is an option but it can release toxic compounds\(^10\), leading to extra costs for gas cleaning processes. A number of works have been carried out using waste glycerol from biodiesel production as feedstock to produce value-added products such as acetyl, 3-hydroxypropanoic acid, glycerol carbonate or hydrocarbons\(^11\) via either biological\(^12,\)\(^13\) or chemical processes.\(^14-17\) However, these methods have major issues with reactor fouling, making them largely uneconomical. Using untreated waste glycerol in biological processes inhibits activities of microorganisms due to the presence of alkaline hydroxides\(^18\) and soap, making biological methods ineffective.\(^15\)

Converting pure glycerol to acrolein\(^19\), acetyl and propylene glycol\(^20\) was examined at a temperature range of 240-305 °C. Despite many methods for producing gas phase products from waste glycerol being known,\(^11-16,\)\(^19\) very little work exists for direct conversion of untreated waste glycerol to liquid products. Therefore, if untreated waste glycerol can be utilised for high-valued liquid products or hydrogen at mild conditions with high yields, it could not only improve the economics of such processes and biodiesel production but also contribute to waste management strategies.

Plasma, the 4\(^{th}\) state of matter, contains electrically excited species such as energetic electrons, radicals, ions and excited molecules. Based on the relative temperatures of the electrons, ions and neutrals, plasmas are classified into "thermal plasma" and "cold plasma". In a thermal plasma, the gas bulk temperature (\(10,000-100,000\) K) is approximately equal to the temperature of the electrons, which is not chemically selective but suitable for hazardous waste treatment\(^21\) and radioactive waste treatment.\(^22\) In contrast, in cold plasma, the bulk temperature is close to ambient but the average electron temperature is in a range of 10,000 - 100,000 K, equivalent to an electron energy of 1-10 eV. Therefore, cold plasma is suitable for catalytic chemical reactions. The cold plasma allows the process to be optimised by changing the reactor design, carrier gas, packing material, applied voltage and frequency. Cold plasma is also highly versatile, and can tolerate a very wide range of feedstocks without significant fouling occurring. The ability to tune the process allows the desired product(s) to be selected more easily than other processing methods. Cold plasma has also been successfully used for dry reforming of methane\(^23-25\) and synthesizing nanomaterials\(^26-28\). Certain types of cold plasma, such as dielectric barrier discharge (DBD)\(^29\), are resistant to fouling because the electrodes are isolated from the reaction mixture\(^30,\)\(^31\) and catalysts can be easily incorporated in a discharge gap. DBD reactors have been studied at industrial scales for ozone generation\(^32\). Using cold plasma to remove oxygen from bio-oil was tested previously.\(^29,\)\(^33\) Zhu et al. carried out the conversion of pure glycerol using cold plasma to hydrogen and carbon monoxide.\(^34\) Additionally, since cold plasma has distinctive thermodynamic behaviour\(^35\) and its properties are altered by operating conditions and reactor configuration\(^36,\)\(^37\), the process can be easily tuned to select for any given desired product(s). In the presence of a catalyst, the product distribution can be controlled to a degree that thermal reactors cannot achieve. Potentially, one component could be decomposed without
affecting the other components in the reactor via control of the plasma properties, which could simplify downstream processing. Therefore, the aim of this work is to investigate the potential of cold plasma and the synergetic effect of cold plasma and packing materials/catalysts in valorising waste glycerol obtained from the biodiesel production process. In order to tune the products, a full understanding of the effect of operating conditions on the process such as carrier gas and plasma power is crucial.

Materials and Methods

Materials

The waste glycerol was kindly donated by Harvest Energy at Seal Sands, Teesside, UK. A Thermoscientific X series ICP-OES was used to determine the concentration of metal in the sample. The sample contained more than 20 elements, of which potassium, sodium and calcium contributed a large percentage, approximately 4.06 wt%, 0.21 wt%, and 0.03 wt% respectively while the others were at ppm levels. The presence of these elements would potentially either foul catalysts in contact with the waste glycerol or act as catalysts for decomposition. The water content of the waste glycerol was 9.45±0.05 wt % determined by Karl-Fischer titration.

The CHN analysis of the waste glycerol sample was performed using a Carlo Erba 1108 Elemental Analyser according to the standard BS ISO 29541. The sample had an empirical formula of \( C_{H_{2.89}}O_{1.14} \). The higher H/C and O/C ratios in waste glycerol than in pure glycerol were due to high water content and the presence of other oxygenated compounds as a product of biodiesel production. Compositions of the waste were glycerol (58.96 wt%), fatty acids (FFA, 33.38 wt%), glycerides (2.13 wt%) and some metal salts as shown in Table 1.

|          | wt%, dry basis |
|----------|----------------|
| Glycerol | 58.96          |
| FFA      | 33.38          |
| Glycerides | 2.13       |
| Methanol | 1.18          |
| Potassium| 4.06          |
| Sodium   | 0.21          |
| Calcium  | 0.03          |
| Others   | 0.05          |

Table 1: Waste glycerol composition

Hydrogen, nitrogen and helium used in this work were high purity gases (>99.999% purity, BOC Ltd.). Barium titanate (BaTiO\(_3\)) beads (99% purity obtained from Alfa Aesar) had a particle size range of 0.5-1 mm. Nickel on supporting alumina (Ni/Al\(_2\)O\(_3\)) was synthesized from high surface area alumina pellets (180 m\(^2\)/g surface area purchased from Alfa Aesar) and nickel nitrate hexahydrate (99.9% purity obtained from Sigma Aldrich) via a wet impregnation method proposed by Bartholomew and Farrauto. Approximately 100 g of Al\(_2\)O\(_3\) pellets was added to 100 ml of 1M solution of nickel nitrate hexahydrate. The mixture was
stirred vigorously at 60 rpm for 1 hour to remove air bubbles. The pellets were extracted and dried in a furnace set at 110 °C for 24 hours. The dried sample was calcinated at 550 °C in air for 5 hours and then hydrogenated at a hydrogen flow rate of 20 ml/min and 550 °C for 24 hours to reduce nickel oxide to nickel. The sample was reduced to 0.5-1 mm in size.

**Experimental Method**

A schematic setup is shown in Figure 1. The plasma reactor was a coaxial type dielectric barrier discharge reactor with a discharge gap of 1 mm and a plasma zone of length 12 cm, providing a total volume of 11.17 cm³. Plasma power supplied to the reactor was varied up to 50 W, at a frequency of 22 kHz. The outer electrode was galvanised steel wire mesh, while the inner electrode was 1 mm thick aluminium foil inside a quartz glass cover. The liquid waste glycerol flow rate was controlled using a syringe pump (errors: ±0.01 ml/min) while the gas flow rate was controlled using a Bronkhorst mass flow controller (errors: ± 0.03 ml/min).

Prior to each experiment, the reactor was continuously purged by a selected gas (hydrogen, helium or nitrogen) for 30 minutes to ensure the system was air-free (confirmed by GC analysis). As soon as the system was air-free, the gas flow rate was adjusted to a desired flow rate. A known flow rate of liquid waste glycerol was continuously injected and mixed with the selected carrier gas at a T-mixer (Figure 1) to obtain consistent slug flow behaviour into the plasma zone. The volumetric ratio of gas to liquid was fixed at 40:1 (v/v) to ensure that liquid was constantly covering the inner electrode, while preventing the reactor from flooding with liquid. Each experiment was repeated at least three times for reproducible purposes.

The outlet reactor was fitted to two condensers cooled at 60 °C and 0 °C to collect liquid products. The gas was collected and analysed online every 15 minutes for 100 minutes. The liquid was collected at the end of the run for off-line analysis and for determining its yield, and the gas yield determined by relative flow rates in and out of the reactor.
Figure 1: Experimental setup for cold plasma assisted waste glycerol decomposition

Analysis

Non-condensable gas outflowing directly from the quenching system was analysed online using a 3 channel Varian 450- Gas Chromatogram (GC). The GC was equipped with 2 ovens, 5 columns, 1 Thermal conductivity detector for permanent gases and 2 flame ionisation detectors for hydrocarbons and alcohols. One oven housed 3 columns (Hayesep T 0.5 m x 15 m x 1/8" ultimetal, Hayesep Q 0.5 m x 1/8" ultimetal and Molsieve 13 m x 1.5 m x 1/8" ultimetal) for permanent gas separation. The second oven housed a CP-SIL 5CB FS X.25 column for hydrocarbon analysis and a CP-WAX 52CB FS 25 m X 0.32 mm (1.2 μm) column for alcohols. The liquid yield was determined by comparing the rate of liquid input to the reactor and the volume of liquid collected at the outlet.
Quantitative analysis of the liquids was performed using a GC-MS equipped with an elite-5 HP capillary column using a heating profile: at 50 °C held for 4 minutes, increased to 180 °C at 15 °C/min, then 7 °C/min to 230 °C, then 10 °C/min to 340 °C and held for 25 minutes. The identified compounds were quantified using a HP6890 GC with an elite-5 HP capillary column with helium as carrier gas. Glycerol and glycerides content was determined according to BS EN 14105-2011.

FTIR analysis was also used to identify functional groups in the liquid fraction, and to confirm the results of GC analysis. FFA content was determined by titration of 0.05 ml of waste glycerol diluted to 2 ml in chloroform containing a pH indicator solution with 0.05 M NaOH in chloroform. Water content in the liquid fraction was determined using Karl-Fischer titration, in an automatic C30 Compact Karl Fischer Coulometer (errors: ± 0.03 wt%)

The conversion of waste glycerol (X) is defined as:

\[ X (%) = \frac{\text{mass waste glycerol fed into the system} - \text{mass unreacted waste glycerol out}}{\text{mass of waste glycerol fed into the system}} \times 100 \]

Where unreacted waste glycerol means the mass of glycerol, FFA, and glycerides remaining in the output stream. Conversion is therefore the total conversion of glycerol, glycerides and FFA to other species.

The process yields are defined as:

\[ \text{Yield of component i (wt%) = } \frac{\text{mass of component i}}{\text{mass of waste glycerol fed into the system}} \times 100 \]

Results and discussion

Effect of operating conditions in the presence of cold plasma on waste glycerol conversion

Table 2 shows that increasing plasma power increased the conversion of waste glycerol. This is due to high energy level electrons contributing to the collisions with gas molecules, creating different energy levels of excited species\(^{37}\). However, the degree of conversion and product yields strongly depends on the carrier gas. The degree of decomposition was in the order: He > H\(_2\) ~ N\(_2\) for FFA but N\(_2\) >> He > H\(_2\) for glycerol. Therefore, if acetol is the desired product, the process should be operated in N\(_2\) environment whereas H\(_2\) and He are the preferred choice of carrier gas if hydrocarbon gases are desired.

Purification of liquid products such as acetol and other products (formic acid and propenal) from unreacted feedstock would be straightforward due to the large differences in boiling points of the compounds\(^{40}\). Other methods such as solvent extraction\(^{41}\) and membranes\(^{42}\) can be also applied.

It is known\(^{43}\) that in N\(_2\) plasma environment, excited nitrogen atoms and molecules (N\(^*\) (\(^4\)S, \(^2\)D, \(^2\)P) and N\(_2\) (\(^1\)Σ\(_u^+\)) were generated. These excited states were generally quenched rapidly at atmospheric pressure and are unlikely to contribute significantly to the reaction, with the possible exception of the triplet meta-stable state of nitrogen, N\(_2\) (\(^3\)Σ\(_u^+\)) and excited nitrogen atoms, N\(^*\) (\(^2\)D), which could initiate the decomposition of glycerol. The wide range of excited states offers a wide range of available energies,
permitting a greater variety of reactions.\textsuperscript{44} Helium, with its very high energy excited state (>19 eV\textsuperscript{45}), the highest first excited state possible of any element, produces some extremely energetic species that can allow reactions that are otherwise impossible. Hydrogen has a low energy excited state (around 3.7 eV\textsuperscript{46, 47}) and is easily converted into hydrogen radicals, allowing rapid hydrogenation.

Table 2 shows that up to 91 % waste glycerol was converted in nitrogen plasma at 50 W and the yield of acetal was high at all tested powers. The glycerol content in waste glycerol was mainly converted into acetal at 50 W in nitrogen plasma. A 22 % reduction in acetal yield (decreased from 44.91 wt% to 34.92 wt%) when increasing power from 10 W to 30 W could be due to the instability of this compound\textsuperscript{20}, which decomposed further to form formic acid (5.67 wt% at 30 W), methane and CO. At 50 W, no formic acid was observed but a significant amount of CO\textsubscript{2} was formed. This can be explained due to formic acid decomposing further to CO\textsubscript{2} at high powers. It can be also concluded that the rate of acetal formation is faster than its decomposition at high plasma powers. It is also observed that in a nitrogen environment, hydrogen production increased with increasing power. This could be explained due to the coupling effect of small hydrocarbons i.e. C\textsubscript{1}-C\textsubscript{2} into C\textsubscript{3}-C\textsubscript{4}.

A significant amount of CO and hydrocarbons (mainly C\textsubscript{2}) were formed in helium plasma (Table 2). Acetal yield decreased with plasma power from 25 wt% at 10 W to 6 wt% at 50 W. The lower yield of acetal than that in the nitrogen environment could be because the high energy level of excited helium cleaves strong chemical bonds. Acetal decomposition generates CO, resulting in at least 145 % more CO produced than the other carrier gases under any conditions. However, a low conversion of glycerol molecules was observed because only a small fraction of excited helium is formed due to the distribution of electron energy\textsuperscript{35}.

In contrast, in a hydrogen environment, the conversion was mainly from the decomposition of FFA in raw waste glycerol to form mainly hydrocarbons and oxygenated compounds of which more than 60 % of the gaseous products were C\textsubscript{1}-C\textsubscript{2}. This can be explained by the low energy level of excited hydrogen and abundant hydrogen radicals in the system. A high yield of formic acid obtained at 50 W (21 wt%) could be the result of stabilising COOH radicals derived from FFA decomposition. No CO\textsubscript{2} and only a small amount of CO (4.7 wt%) observed at 50 W was due to the decomposition of acetal. \textsuperscript{4, 48}

Table 2: Yields and properties of products obtained from liquid waste glycerol decomposition in the presence of cold plasma at atmospheric temperature and pressure without catalysts under different types of carrier gas with a residence time of 16 seconds.
Figure 2 shows that OH groups in the liquid phase were mostly converted to ketones instead of to water as reflected by the trend of water content presented in Figure 3. This can be seen from the significant changes in the O-H, C-H and C=O peaks at 3300 cm\(^{-1}\), 2900 cm\(^{-1}\) and 1700 cm\(^{-1}\) respectively. A slight increase in the C-H peak (Figure 2a) could be a result of the hydrogenation. The hydrogenation of glycerol would require the replacement of a hydroxyl radical with hydrogen or hydrogenation of C=C bonds formed from removal of alcohol groups to other oxygenated groups. All the peaks in the range 700-1500 cm\(^{-1}\) decreased after plasma treatment, which is an indicator of shorter chain hydrocarbons in the products. This is supported by the formation of hydrocarbons in the gas phase. The same behaviour was observed in nitrogen and helium plasma as shown in Figures 2b & 2c.
Figure 2: FTIR spectra of the liquid phase before (raw waste glycerol) and after (a) hydrogen; (b) nitrogen and (c) helium purged plasma.
Figure 3: Water content of waste glycerol feedstock and liquid products obtained at various treatment conditions without catalysts at atmospheric temperature and pressure with a 16 second residence time.

To date, direct conversion of waste glycerol to high value added liquid products has not been reported. However, conversion of waste glycerol into gases at high temperatures (650-800°C) has been studied.\textsuperscript{49,50} Dehydration of pure glycerol under high temperature water and/or high pressure of CO\textsubscript{2} via catalytic reactive distillation was reported\textsuperscript{20, 51} with the yield of acetal varying from 26-60 wt% depending on catalysts over >1 hour reaction time. By using cold plasma in this study, without a catalyst and at ambient conditions, 52 wt% acetal from waste glycerol was obtained at around 16 second residence time alongside 14.78 wt% hydrocarbon gas (C\textsubscript{1}-C\textsubscript{4}), 2.72 wt hydrogen and 9.90 wt% CO. Based on the trend of acetol and gases (hydrocarbons and CO) with cold plasma power, it can be concluded that the acetol formation pathway in cold plasma is similar to that obtained in thermal processing, where glycerol dehydrates secondary OH to form acetol. Propenal is the product of the dehydration of the primary OH group.\textsuperscript{52} Propenal could decompose to ethene and formate radicals\textsuperscript{19, 53}, of which the latter can dehydrogenate further to carbon monoxide.\textsuperscript{54, 55} In this study, propenal was not detected except in the presence of hydrogen, which is due to the instability of aldehydes in cold plasma.\textsuperscript{56} It was also noted that the water content decreased in the presence of plasma, which suggests that OH radicals are formed from the water and maintain an equilibrium.

Formic acid and hydrocarbons were the products of FFA decomposition.\textsuperscript{57} The formic acid is likely then dehydrogenated to CO\textsubscript{2}, particularly in the absence of hydrogen radicals. However, from the experimental data, no correlation between FFA content and CO\textsubscript{2} formation suggests that CO\textsubscript{2} formation in nitrogen is dominated by another reaction. The OH radicals formed would react with carbon monoxide, and in turn dehydrogenate to carbon dioxide.\textsuperscript{57-60} This only occurs in nitrogen, which suggests that the energy...
required for this pathway is closest to the energy of nitrogen radicals. Formic acid is generated under certain conditions at yields of up to 21 wt%. The proposed mechanism for cold plasma assisted glycerol decomposition is shown in Figure 4 below.
Figure 4: Proposed mechanism of cold plasma assisted waste glycerol decomposition

**Effect of packing material and catalyst in the presence of cold plasma**

Packing materials (e.g. BaTiO$_3$) had a slight effect on the conversion but enhanced the decomposition of acetol into gaseous products such as hydrocarbons and CO (Table 3). However, the degree of decomposition was lower for Al$_2$O$_3$ than BaTiO$_3$. This is because the packing materials and their properties alter the electric field, consequently electron energy by varying the discharge gap ($d$) and/or the gas density $n$ (proportional to gas pressure).$^{61-62}$ When introducing packing beads, the discharge gap in the DBD reactor is the gap between the beads, which is much smaller than the gap without packing materials (1.5 mm), thereby enhancing local electric fields. This occurs due to refraction of the electric field as shown in Figure 5, making the local electric field non-uniform and stronger than the external sources. Furthermore, the strength of electric field near the contact points between the beads can be significantly higher than that in the void by a factor of 10–250 depending on the shape, porosity, and permittivity of the beads.$^{47}$ An increase in dielectric constant/permittivity of materials can result in a further increase in electric field, particularly near the contacting points.$^{62}$
When the catalyst Ni/Al₂O₃ was embedded in the plasma zone, up to 99% waste glycerol was converted into gaseous products. Ni/Al₂O₃ is a common hydrodeoxygenation catalyst and therefore was used to examine the ability of integrated hydrogen production from plasma and deoxygenation of the liquid at near ambient conditions. When a catalyst is introduced to the plasma, chemical reactions in the plasma occur in gas phase reactions and heterogeneous reactions on the catalyst surface. Therefore, a catalyst may significantly influence the plasma chemistry. The interactions between DBD plasma and catalysts are complex as the catalyst with its dielectric properties could modify the electric field and the electric field may affect catalyst effectiveness, i.e. altering the surface properties of the catalyst to allow operation at much lower temperatures and more effectively. These plasma-catalyst interactions have been studied for CO₂ decomposition. The conversion was slightly reduced when increasing power to 50W due to the formation of plasma arcs.

Table 3: Effect of packing materials and catalyst on conversion and product distribution under a nitrogen environment at 6 second residence time

| Packing material | No packing | BaTiO₃ | Ni/Al₂O₃ | Al₂O₃ |
|------------------|------------|-------|----------|-------|
| Plasma power, W  | 50         | 10    | 30       | 50    |
| Conversion, %    | 56.98±2.03 | 26.85±4.7 | 45.29±5.9 | 60.97±6.2 |
| Total gas yield, wt% | 27.6±0.97  | 18.92±1.82 | 44.79±4.2 | 60.71±5.50 |
| CO₂              | 8.96       | 6.49  | 8.23     | 13.80  |
| H₂               | 3.35       | 0.24  | 1.50     | 2.45   |
| CH₄              | 3.66       | -     | 0.44     | 0.87   |
| CO               | 7.63       | 0.96  | 7.45     | 12.21  |
| C₂               | 2.46       | 4.43  | 11.44    | 14.72  |
| C₃               | 0.93       | 2.93  | 4.17     | 6.74   |
| C₄               | 0.61       | 3.87  | 6.03     | 7.59   |
| C₅               | -          | -     | 5.52     | 2.32   |
| Liquid products, wt% | 29.29±1.67 | 7.55±2.88 | 0.50±1.19 | 0.26±0.70 |
| Propenal         | -          | 0.23  | 0.05     | 0.04   |
Figure 6 shows that the water content in the liquid was around 50% lower than that in the feedstock and remained almost constant at 4 wt% with increasing power in the case of BaTiO$_3$ and Al$_2$O$_3$. This is because the decomposition of H$_2$O into OH radicals and generation of water via dehydration pathways were in equilibrium. With Ni/Al$_2$O$_3$, the water content remained similar to that in the raw material up to 25 W and then sharply decreased to zero at 30 W. This was due to the consumption of OH radicals by hydrocarbons and ketones, followed by decomposition to form carbon oxides. An increase in the water content at powers above 30 W was due to plasma arcing (heterogeneous environment).

| Acetol | 29.29 | 7.32 | 0.45 | 0.22 | 6.27 | 0.19 | - | 3.71 | 6.47 | 6.61 |
|--------|-------|------|------|------|------|------|---|------|------|------|
| Glycerol | 34.52 | 64.06 | 47.60 | 35.19 | 52.81 | 0.81 | 15.24 | 58.26 | 46.22 | 31.47 |
| Fatty acids | 5.17 | 8.21 | 6.37 | 3.47 | 2.01 | 0.04 | 0.60 | 31.54 | 30.34 | 25.89 |
| Glycerides | 3.42 | 0.88 | 0.75 | 0.37 | 0.17 | 0.01 | 0.08 | 2.21 | 2.01 | 1.78 |

| Plasma Power (W) | Raw | 5 | 10 | 20 | 25 | 28 | 30 | 40 | 50 |
|------------------|-----|---|----|----|----|----|----|----|----|
| Water content (wt%) | 12 | 10 | 8  | 6  | 4  | 2  | 0  | 2  | 4  |

Figure 6: Water content versus plasma power for packing materials and catalyst Ni/Al$_2$O$_3$ at 4 second residence time

It was found that after 1 hour operating time, the conversion of waste glycerol in the presence of Ni/Al$_2$O$_3$ significantly decreased, by approximately 50%. This is due to fouling, which is in agreement with previous studies. The same behaviour was observed for Al$_2$O$_3$ but not for BaTiO$_3$. The spent and fresh Ni/Al$_2$O$_3$ catalyst was then analysed using BET, SEM with EDX and XRD. For the fresh catalyst, SEM-EDX analysis (Figure 7a) showed large particles of diameter of 0.5-1 mm with mainly Ni, Al and O elements with a ratio of O/Al comparable to that reported in literature. In contrast, SEM images of the spent Ni/Al$_2$O$_3$ catalyst show rounded surfaces with very few pores and bubble like nodes are visible on the material’s surface (Figure 7b). From XRD analysis (Figure 7d), the spent catalyst had an additional peak at 21°, indicating a partial coverage of solid carbon on the surface. A very high degree of fouling which occurs within the 1 hour running time is carbon based, but contains significant
potassium content (up to 15.5 wt%). The nodules form at the areas where carbon accumulates. The resulting fouling on these points retains OH groups so more waste glycerol adheres to it, building up into a nodule. The pores are largely clogged with waste glycerol and some deposits could be formed internally. The sample was also regenerated successfully and analysed, which showed no significant differences from the initial catalyst (Figure 7c) as evidenced by the similar conversion and product distribution obtained over the regenerated catalyst. When the spent catalyst was regenerated at 550°C in nitrogen, the additional peak at 21° disappeared. It was found that spent catalysts can be regenerated by cold plasma at lower temperatures with shorter residence times than by conventional regeneration methods. However, this is not in the scope of this study.

Figure 7: (a,b,c) SEM image of at x6500 magnification of (a) fresh, (b) spent and (c) regenerated catalysts and (d) XRD of fresh, spent and regenerated Ni/Al₂O₃.
Conclusions
In this study, the influence of plasma power, carrier gas, packing material and catalyst on waste glycerol conversion was studied. The carrier gas was found to be a significant factor in the conversion and product distribution. Hydrogen carrier gas favours the formation of hydrocarbon products and propenal, and preferentially decomposes FFA molecules. Nitrogen carrier gas produces the highest yield of acetol due to preferentially decomposing glycerol. Helium carrier gas favours carbon monoxide and preferentially decomposes glycerides. The effect of reaction time was more pronounced than packing materials. Approximately 99% waste glycerol was converted into gaseous products at 30 W, of which 55 mol% (7.02 wt%) was hydrogen when using Ni/Al2O3. Ni/Al2O3 catalyst deactivated quickly within 1 hour operating time due to the deposition of carbons and impurities from the waste glycerol feedstock i.e. potassium. However, the catalyst can be regenerated easily in 550 °C oxygen free nitrogen. This study reveals opportunities to convert waste into high added value products over a short period of time at near ambient conditions with the products easily tuned according to demand.

Conflicts of interest
There are no conflicts to declare.

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