

## Catalytic steam reforming of biodiesel as a means of renewable hydrogen production.

Gaurav Nahar<sup>1\*</sup>, Valerie Dupont<sup>1</sup>, Emiliana Dvininova<sup>2</sup>

<sup>1</sup> Energy Resources Institute, The University of Leeds, LS2 9JT, UK

<sup>2</sup> MEL Chemicals, PO BOX 6, Lumns Lane, Swinton, Greater Manchester M27 8LS, UK

\*corresponding author: ganahar@gmail.com

### Introduction

Hydrogen production from fresh vegetable oils like sunflower, canola and rapeseed oils using nickel based catalyst has been reported by Markevich et al[1]. Similarly the use of waste cooking oil and palm oil fatty acid distillates for hydrogen production were reported by Pimenidou et al and Shotipruk et al [2-4]. Hydrogen production from bio-diesel is relatively new and only very few conceptual and catalytic investigations have been reported. Hydrogen production via catalytic steam reforming of biodiesel over Ni supported ceria-zirconia catalyst was evaluated.

### Materials and Methods

The Ni supported ceria zirconia catalyst was prepared using wet impregnation and dry impregnation method. A 17 wt % ceria doped zirconia [(MELCat XZO1580/01) was used as catalyst support provided by MEL Chemicals, UK. The catalytic support is a ceria stabilized tetragonal zirconia and has an average particle size of 5µm and high purity. Nickel nitrate solution was used to obtain the desired nickel loading of 10-30 wt %. The experiments were run in a fixed bed continuous-flow reactor equipped with separate vaporizers for biodiesel and water. Experiments were at molar steam to carbon (S/C) of 3, 650°C and weight hourly space velocity (WHSV) of 3.18 h<sup>-1</sup>. Biodiesel and water were delivered individually using two syringe pumps and the gases were analyzed using a Varian CP 4900 micro-GC equipped with two TCD detectors using molecular sieve and polar plot columns. Surface area, pore-size and pore volume analysis of the catalyst were determined using Quantachrome NovaWin surface area and porosity analyzer. X-ray diffraction of the catalyst was performed using a Bruker D8.

### Results and Discussion

X-ray diffraction and surface area analysis of the Ni supported on Ce-ZrO<sub>2</sub> catalysts at different Ni loadings is provided in Table 1.

**Table 1.** X-ray diffraction, surface area and pore-size analysis of catalyst prepared wet impregnation method.

Ni Loading	BET (m <sup>2</sup> /g)	Crystallite size, XRD (nm)	Pore size (nm)	Pore volume cc/g	Ni dispersion (%)
None	380 (fresh)	-	-	0.37	0
10 wt %	55.89 <sup>a</sup> 59.70 <sup>b</sup>	11.41 <sup>c</sup> 15.49 <sup>d</sup>	4.692	0.135	6.35
20 wt %	53.96 <sup>a</sup>	11.3 <sup>c</sup>	4.796	0.133	

	58.37 <sup>b</sup>	37.28 <sup>d</sup>			2.71
30 wt %	48.76 <sup>a</sup> 53.97 <sup>b</sup>	11.3 <sup>c</sup> 33.9 <sup>d</sup>	4.475	0.122	2.98

a- BET surface area, b-BJH adsorption surface area-support crystallite size, and d-NiO crystallite size.

The 10 wt % Ni/Ce<sub>0.12</sub>Zr<sub>0.88</sub>O<sub>2</sub> was selected for biodiesel steam reforming based on its smaller NiO crystallite size and higher dispersion. The catalyst performance (Table 2) was evaluated for 2 hrs. Carbon monoxide, carbon dioxide and methane selectivities of 63.60, 56.64 and 2.10 % respectively, were found during the experiment. Small amount of alkenes and alkanes i.e. ethylene, propylene and ethane were also measured during the evaluation.

**Table 2 .** Catalytic performance of steam reforming of biodiesel using (S/C) of 3, at 650°C and WHSV of 3.18 h<sup>-1</sup>. The vaporizer temperatures for biodiesel and water were set at 190 and 170°C respectively.

	H <sub>2</sub> yield (wt % of biodiesel feed)	Biodiesel conversion to C-gases	Steam conversion (%)	CO/CO <sub>2</sub> ratio	Selectivity to H <sub>2</sub> amongst H-gases (%)
Experimental	27.82	96.1	41.3	0.51	98.1
Equilibrium	29.75	100	47.5	0.71	98.4

### Significance

Steam reforming of biodiesel over 10 wt % Ni/Ce<sub>0.12</sub>Zr<sub>0.88</sub>O<sub>2</sub> catalyst yielded outputs close to chemical equilibrium for the duration of the experiments of 2h.

### References

- [1] Markevich, M.; Farriol, X.; Medina, F.; Montané, D. *Ind. & Eng. Chem. Res.* (2001), 40, 4757.
- [2] Pimenidou, P.; Rickett, G.; Dupont, V.; Twigg, M.V. *Bioresour Technol.* (2010), 101, 6389.
- [3] Pimenidou, P.; Rickett, G.; Dupont, V.; Twigg, M.V. *Bioresour Technol.* (2010), 101, 9279.
- [4] Shotipruk, A.; Assabumrungrat, S.; Pavasant, P.; Laosiripojana, N. *Chem. Eng. Sci.* (2009), 64, 459.