



## Sonochemically Assisted Ni-Ce Oxide Catalyst for Gasification of Coconut Shell

Y.C. WONG<sup>1,2,\*</sup>, M. MOHAMED<sup>1</sup> and Y.H. TAUFIQ-YAP<sup>2,3</sup>

<sup>1</sup>Faculty of Agro Based Industry, Universiti Malaysia Kelantan, Locked Bag 100, 17600 Jeli, Kelantan Darul Naim, Malaysia

<sup>2</sup>Centre of Excellence for Catalysis Science and Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia

<sup>3</sup>Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia

\*Corresponding author: Fax: +60 99477022; Tel: + 60 994771108; E-mail: yeeching@umk.edu.my

Received: 15 June 2015;

Accepted: 27 August 2015;

Published online: 5 December 2015;

AJC-17656

Catalysts containing mixtures of nickel oxide and cerium oxide with ratio, 1:1 were prepared by the sonochemical treatment. The sonication was prolonged for 15, 45 and 75 min, different for each of the catalyst prepared supported by alumina. The resultant catalysts were characterized using X-ray diffraction, scanning electron microscope, Brunauer-Emmet-Teller surface area measurement ( $S_{BET}$ ) and temperature programmed reduction in  $H_2$ . The syngas production was detected using temperature programmed gasification and it was done under 5 % oxygen in helium. The coconut shell in powder form (3  $\mu$ m) was used as a feedstock. X-ray diffraction patterns shows that all of the catalyst was perfectly matched to the XRD patterns standard of NiO, CeO<sub>2</sub> and alumina, indicating that the catalyst produce through this method were in high purity. Catalyst with 45 min sonication shows the highest syngas production ( $H_2/CO$ ) with ratio 0.76 followed by 15 and 75 min with 0.66 and 0.35, respectively. Compared to the standard optimum ratio of syngas can be used for production of acetic acid and acetyl oxide.

**Keywords:** Syngas production, Biomass gasification, Mixed nickel oxide, Cerium catalyst.

### INTRODUCTION

Biomass is referred to all form of plant materials including husk, shell, bunch and others [1]. Biomass is one of the main resources of renewable energy [2]. Gasification of biomass is a thermochemical process [1]. For choosing a suitable feedstock for gasification, it is commonly depends on the feedstock abundance and its availability [3].

The feedstock that has special attention in this study is coconut shell in the powder form. It is organic in nature and the shell is the most versatile part of the coconut [4]. In Malaysia, huge amount of coconut shell are generated every years, as it is one of the major crops in this country with 142,000 ha of planted land [5].

The catalyst is used in the gasification process purpose to reduce the temperature for devolatilize biomass sample. For example, without the presence of catalyst, the biomass starts to decompose at 270 °C, while in the presence of catalyst the biomass sample has started decomposing at 225 °C [6].

The purpose of this study is to investigate a potential of syngas production from coconut shell in powder form *via* temperature-programmed gasification process using a mixture of NiO and CeO<sub>2</sub> as a catalyst. Syngas is referred as a mixture of carbon monoxide and hydrogen which is converted from the biomass sources and takes place in a gasifier [7].

### EXPERIMENTAL

**Preparation of biomass:** Coconut shells were collected from the area of Kota Bharu. They were then separated by its husk before sun dried. Coconut shells obtained were further grinded into powder form and further sieve (3  $\mu$ m) before drying in oven at 338 K for 24 h.

**Preparation of mixed nickel oxide and cerium oxide catalysts supported by alumina:** Mixtures of nickel oxide and cerium oxide catalyst were synthesized by mixing NiO (from Hmbg) and CeO<sub>2</sub> (from Merck) in distilled water (100 mL). Ratio of NiO and CeO<sub>2</sub> in each catalyst was constant which is 1:1.

The solutions were then sonicated for 15, 45 and 75 min, different for each catalyst prepared. The colour of the solid solution was grey and the resultant grey solid (mixture of NiO and CeO<sub>2</sub>) was then recovered using centrifuge technique and subsequently washed sparingly with distilled water and acetone, then oven dried for overnight at 373 K.

The synthesized mixture of nickel oxide and cerium oxide were then added with alumina as a supporter, in distilled water (100 mL). Then, it was stirred on a hot plate for 1 h by using magnetic stirrer.

The solid was again recovered by centrifuge technique, subsequently washed sparingly with distilled water and acetone

then oven dried for overnight at 373 K, yielding a homogeneous catalyst.

**Catalysts characterization:** X-ray diffraction (XRD) analysis was carried out by using a Shimadzu diffractometer model XRD 6000.

The LEO 1455 variable pressure scanning electron microscope (SEM) was used to observe the morphology of the catalysts. The accelerating voltage applied was 20 kV. The BALTEC 005 sputter coater was used to cover the sample with a thin layer of gold. The SEM images were display as a result of secondary and backscattered electron images were produced as they were generated by the electron beam irradiation and collected by the detector.

The surface area of the catalyst studied was measured by using Brunauer-Emmet-Teller (BET) method. It was done by using nitrogen adsorption at 77 K. For each sample analyzed, at least 0.1 g of sample was used.

H<sub>2</sub>-temperature programmed reduction analysis was performed using Thermo Fisher Scientific TPDRO 1100 apparatus equipped with a thermal conductivity detector (TCD).

**Catalysts evaluation:** Temperature programmed gasification (TPG) was carried out by using Thermo Finnigan TPDRO 1100 apparatus online with a mass spectrometer (model Quadstar) that able to detect the output gas composition. The coconut shell gasification was done at temperature range from 50 to 900 °C, with a heating rate 10 °C min<sup>-1</sup>. The temperature was hold for 1 h at final temperature.

The gases that were detected by mass spectrometer were H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> by following its *m/z* 2, 28, 44 and 16, respectively. The ratio by mass of catalyst to coconut shell studied was 1:3.

## RESULTS AND DISCUSSION

**X-ray diffraction (XRD):** The XRD patterns of the catalysts were shown in Fig. 1. All of the catalysts exhibit the characteristics peaks of crystalline CeO<sub>2</sub> (at 2θ angle of 28.8°, 33.4°, 47.8°, 56.7°, 59.4°, 69.8°, 77.0° and 79.4°), NiO (at 2θ angle of 63.1°) and Al<sub>2</sub>O<sub>3</sub> (at 2θ angle of 37.6° and 43.5°).

Although sonication time of the catalyst are different, but the produce catalyst did not cause any changes in terms of the

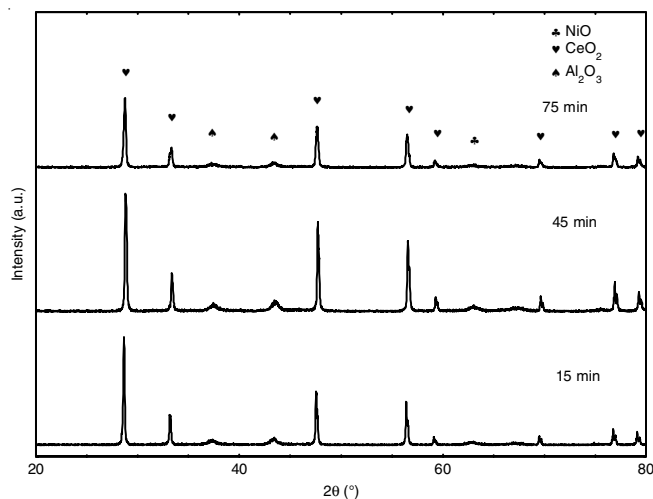


Fig. 1. XRD patterns of mixed metal oxide catalyst with different sonicating time

basic matrix of NiO, CeO<sub>2</sub> and supporter Al<sub>2</sub>O<sub>3</sub>. Therefore, the catalysts produce by sonicating process consist of high purity. This can be further proved that, there are no other impurity crystalline phases are detected in all catalyst samples.

Besides, the size of crystallite was also estimated by the XRD result using Scherrer equation [8],

$$L = K\lambda/\beta \cdot \cos \theta \quad (1)$$

where L = average crystallite size, K = constant which is normally taken as 0.9, λ = X-ray wavelength, β = peak width of the diffraction peak profile at half maximum height and θ can be either in degrees or radians.

The size of 1:1 mixture of NiO/CeO<sub>2</sub> catalyst with sonicating time 15, 45 and 75 min, are 42.75, 33.10 and 27.53 nm, in average respectively (Table-1).

TABLE-1 AVERAGE OF CRYSTALLITE SIZE FROM XRD RESULT (nm)	
Catalyst	Average of crystallite size (nm)
15 min	42.75
45 min	33.10
75 min	27.53

**Scanning electron microscope (SEM):** The surface morphologies of the mixed nickel oxide and cerium oxide catalysts synthesized by sonication method were examined using scanning electron microscope with 5000 magnification (Fig. 2).

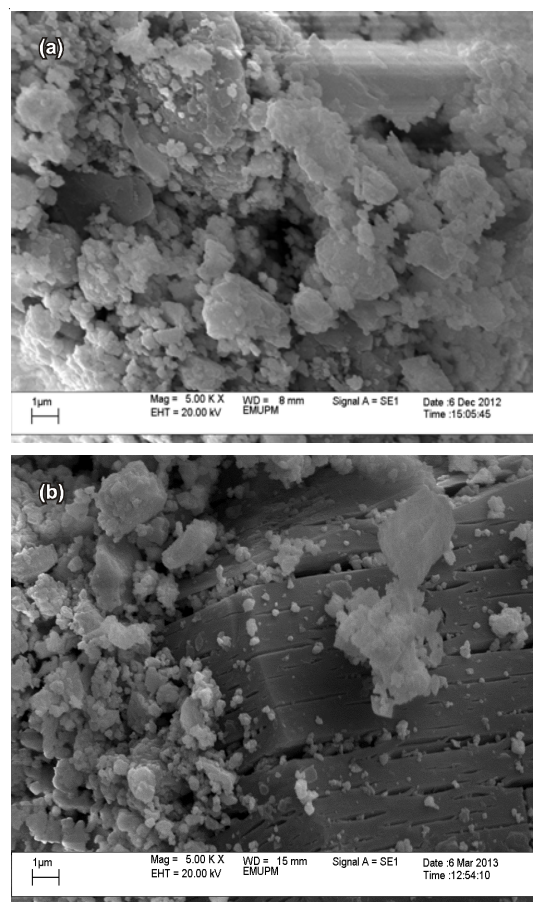


Fig. 2. SEM micrographs of mixed metal oxide catalyst with different sonicating time (a) 45 min (b) 75 min (with 5000× magnification)

The catalyst studied shows their plate-like structure without symmetry staggered to each other. The particles are also shown in agglomerate form.

**Brunauer-Emmet-Teller surface area measurement ( $S_{\text{BET}}$ ):** The  $S_{\text{BET}}$  result for 1:1 mixture of NiO/CeO<sub>2</sub> catalysts with sonicating time 15, 45 and 75 min were shown in Table-2. It shows that catalyst with sonicating time 45 min has the highest surface area which is 102.965 m<sup>2</sup>/g compared to 53.414 and 52.011 m<sup>2</sup>/g of catalyst with 75 and 15 min, respectively.

TABLE-2  
BET SURFACE AREA OF MIXED METAL OXIDE CATALYST WITH DIFFERENT SONICATING TIME

Catalyst	Surface area (m <sup>2</sup> /g)
15 min	52.011
45 min	102.965
75 min	53.414

Basically, a higher surface area is close related to its smaller particle size of a sample [9]. Nevertheless, based on this study, both surface area and particle size estimated by XRD result was not related at all. This may be due to the nature of the metal oxide catalyst itself which is in the mixed phase.

**Temperature programmed reduction (TPR in H<sub>2</sub>/Ar):**

The reduction profiles of 1:1 mixture of NiO/CeO<sub>2</sub> catalysts with sonicating time 15, 45 and 75 min were demonstrate in Fig. 3. There was a maximum peak exhibited by each catalyst. The rate of hydrogen consumption was at 432, 422 and 403 °C for 15, 45 and 75 min, respectively. The amount of oxygen removed by the reaction with H<sub>2</sub> for this 1:1 mixture of NiO/CeO<sub>2</sub> catalyst with sonicating time 15, 45 and 75 min were 0.43, 0.36 and 0.25 × 10<sup>22</sup> atoms g<sup>-1</sup>, respectively as shown in Table-3.

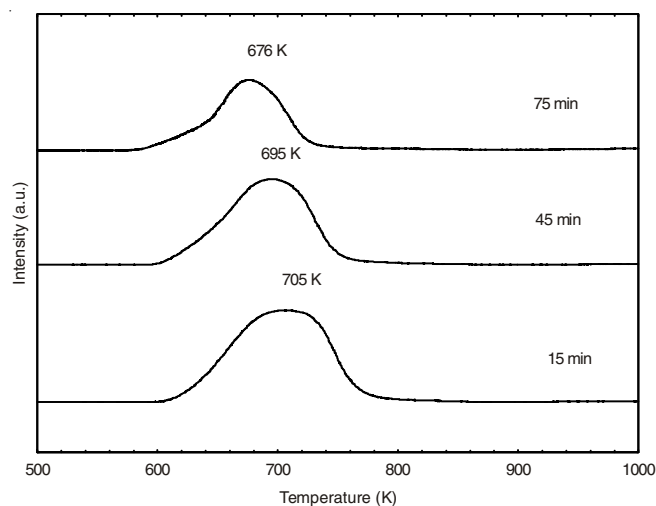


Fig. 3. Temperature programmed reduction profiles for the mixed metal oxide catalyst with different sonicating time, 15, 45 and 75 min

From the result obtained, it is noticed that oxygen removed become decrease when the sonicating time increase. This is due to the Ni presence in the catalyst which will be dispersed more evenly on the surface of CeO<sub>2</sub> as the time of sonicating increase. Therefore, it is not possible for CeO<sub>2</sub> to release its oxygen when combining with NiO because CeO<sub>2</sub> reduction hidden as its external surface is significantly lowered by the presence of Ni [10].

TABLE-3  
TOTAL AMOUNT OF OXYGEN REMOVED FROM MIXED METAL OXIDE CATALYST WITH DIFFERENT SONICATING TIME

Catalyst	T <sub>max</sub> (K)	Oxygen atom removed (×10 <sup>-3</sup> mol g <sup>-1</sup> )	Oxygen atom removed (×10 <sup>22</sup> atoms g <sup>-1</sup> )
15 min	705	7.2	0.43
45 min	695	5.9	0.36
75 min	676	4.1	0.25

**Temperature programmed gasification (TPG):** The highest ratio of syngas production (H<sub>2</sub>/CO) was 1:1 mixture of NiO/CeO<sub>2</sub> catalyst with 45 min sonication time which is 0.76, contributed by the higher hydrogen produce, 0.8282 cm<sup>3</sup> if compared to the 1:1 catalyst with 75 min sonicating time which is 0.3558 cm<sup>3</sup> (Table-4). The higher hydrogen produce was due to its higher surface area which is 102.965 m<sup>2</sup>/g (Table-2). Furthermore, the high surface area will also increase the active site of the catalyst. This increasing active site will increase the contact frequency between the catalyst and coconut shell [11]. Hence, hydrogen production becomes increase.

TABLE-4  
SYNGAS AND BYPRODUCT PRODUCE (cm<sup>3</sup>) BY MIXED METAL OXIDE CATALYST WITH DIFFERENT SONICATING TIME

Catalyst	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> /CO
15 min	0.8555	1.2934	3.7274	1.9438	0.66
45 min	0.8282	1.0882	3.0199	1.6895	0.76
75 min	0.3558	1.0204	1.8002	1.3647	0.35

While, 1:1 mixture of NiO/CeO<sub>2</sub> catalyst with sonicating time 75 min produces the lowest ratio of syngas production (H<sub>2</sub>/CO) with 0.35 and this is due to the lowest hydrogen production, 0.3558 cm<sup>3</sup>, if compared to the other sample studied.

According to this study, the more oxygen was removed from the catalyst, the higher tendency of the oxygen to react with carbon and produce CO and CO<sub>2</sub> (reaction 2 and 3 [12]). This is in agreement with the result obtained from temperature programmed reduction in H<sub>2</sub> (Table-3).



## Conclusion

The gasification of coconut shell was carried out by using 1:1 ratio of mixed NiO/CeO<sub>2</sub> catalyst with 15, 45 and 75 min sonication time and coconut shell in powder form (catalyst: biomass = 1:3) at temperature 50 to 900 °C and hold for 1 h at the end temperature. 1:1 mixed NiO/CeO<sub>2</sub> catalyst with sonicating time 75 min, produce the highest syngas (H<sub>2</sub>/CO) ratio, 0.76 due to its higher surface area and high contact frequency between the catalyst and coconut shell. The result also shows that the coconut shell can be gasified using mixed NiO/CeO<sub>2</sub> catalyst with ratio catalyst: coconut shell = 1:3 at temperature range 50-900 °C.

## ACKNOWLEDGEMENTS

This work was supported by Research Grant R/RAGS/A07.00/00457A/002/2012/000093 from the Ministry of Higher Education, Malaysia.

## REFERENCES

1. P.K. Senapati and S. Behera, *Bioresour. Technol.*, **117**, 99 (2012).
2. A. Paethanom, S. Nakahara, M. Kobayashi, P. Prawisudha and K. Yoshikawa, *Fuel Process. Technol.*, **104**, 144 (2012).
3. M. Vaezi, M. Passandideh-Fard, M. Moghiman and M. Charmchi, *Fuel Process. Technol.*, **98**, 74 (2012).
4. S. Husseinsyah, and M.M. Zakaria, *Malaysian Polym. J.*, **6**, 87 (2011).
5. A.T. Mohd Din, B.H. Hameed and A.L. Ahmad, *J. Hazard. Mater.*, **161**, 1522 (2009).
6. J. Chattopadhyay, J.E. Son and D. Pak, *Korean J. Chem. Eng.*, **28**, 1677 (2011).
7. M. Guo, W. Song and J. Buhain, *Renew. Sustain. Energy Rev.*, **42**, 712 (2012).
8. A. Monshi, M.R. Foroughi and M.R. Monshi, *World J. Nano Sci. Eng.*, **2**, 154 (2012).
9. M. Florea, A.-S. Mamede, P. Eloy, V.I. Parvulescu and E.M. Gaigneaux, *Catal. Today*, **112**, 139 (2006).
10. A. Valentini, N. Carreno, L. Probst, A. Barison, A. Ferreira, E. Leite and E. Longo, *Appl. Catal. A*, **310**, 174 (2006).
11. K. Ismail, M.A. Yarmo, Y.H. Taufiq-Yap and A. Ahmad, *J. Hydrogen Energy*, **37**, 3639 (2012).
12. A.G. Buekens and J.G. Schoeters, *Modelling of Biomass Gasification*, Vrije Universiteit Brussel, Brussels, Belgium (1985).