Experimental evaluation and empirical modelling of palm oil mill effluent steam reforming

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ABSTRACT

The current work describes a novel application of steam reforming process to treat palm oil mill effluent (POME), whilst co-generating H_2-rich syngas from the treatment itself. The effects of reaction temperature, partial pressure of POME and gas-hourly-space-velocity (GHSV) were determined. High crystallinity 20 wt%Ni/80 wt%Al_2O_3 catalyst with smooth surface was prepared via impregnation method. Baseline runs revealed that the prepared catalyst was highly effective in destructing organic compounds, with a two-fold enhancement observed in the presence of 20 wt% Ni/80 wt%Al_2O_3 catalyst, despite its low specific surface area (2.09 m^2 g^{-1}). In addition, both the temperature and partial pressure of POME abet the COD reduction. Consequently, the highest COD reduction of 99.7% was achieved, with a final COD level of 73 $\pm$ 5 ppm from 27,500 ppm, at GHSV of 40,000 mL/h.g_{cat} and partial pressure of POME equivalent to 95 kPa at 1173 K. In terms of gaseous products, H_2 was found to be the major component, with selectivity ranged 51.0% −70.9%, followed by CO_2 (17.7%−34.1%), CO (7.7%−18.4%) and some CH_4 (0.6%−3.3%). Furthermore, quadratic models with high R^2-values were developed.

Introduction

In 2016, 17.32 million tonnes of crude palm oil was produced in Malaysia from 5.74 million hectares of oil palm plantation, generating nearly RM65 billion of export revenue for Malaysia [1]. Unfortunately, it comes at a cost of environmental pollution in the forms of palm oil mill effluent (POME). It is a common knowledge that an extrusion of each tonne of palm oil would generate 7-fold amount of POME [2,3]. Alarmingly, POME is polluting water resources, due to its high COD and BOD levels.

The primary POME treating method employed in Malaysia is a low operating-cost open ponding system. This system consists of a series of anaerobic and aerobic ponds. To date, there are more than 85% of the palm oil millers that rely on this conventional method [4], despite that these ponds would

require large land and long retention time (up to months). Furthermore, it has also been proved that ponding system is no longer sufficient in treating POME to the level permissible by authorities [5,6].

Consequently, efforts have been ramped up by researchers to eradicate the aforementioned problems. For example, membrane application was widely investigated due to its perceived high efficiency [3,7,8]. In addition, adsorption process [9], combination of membrane and adsorption processes [10], magnetic field-assisted adsorption process [11] and ultrasound-assisted adsorption [12] were also employed. However, all these innovations only focus on 'treatment', overlooking the potential of generating renewable energy from POME waste.

In recent years, a new paradigm has set in, whereby POME treatment has embraced the concept of "waste-to-wealth". Innovative methods, mainly anaerobic digestion, were engineered to co-obtain biogas from POME [13—17]. Indeed, the Malaysian Government has earmarked POME as a source of green energy production. This culminates in the development of numerous biogas facilities via the introduction of Economic Transformation Programme (ETP − EPP 5). In fact, anaerobic biogas generation facilities were erected in the 57 mills all over Malaysia for on-site thermal energy and electricity generation [18]. In addition to anaerobic process, other processes such as photocatalysis [6,19—23], acidogenesis [24] and hydrolysis [25] have been examined for biogas generation from POME.

Besides biogas, generation of hydrogen from POME was also successfully demonstrated through bioprocesses [26—28]. Likewise, in the current work, syngas with hydrogen as the major component was successfully generated via steam reforming of POME. To our best knowledge, we are the first research group who is pioneering on this technique. Nickel (Ni) metal which is commonly associated with high temperature steam reforming process was employed herein as a catalysing metal. Based on our previous report [29], H_2-rich syngas was successfully generated from the steam reforming of POME waste over the Ni-catalyst. As an extension from the previous study, this study investigates the effects of reaction temperature, partial pressure of POME and gas-hourly-space-velocity (GHSV) on the COD reduction and gaseous product distributions. Significantly, empirical mathematical models were also developed from the resulting investigation for predicting the POME treatment trend and also to capture the profile of product distributions.

Methods

Sampling and preservation of POME

Fresh POME was collected from a waste-discharge point of a palm oil mill located in Kuantan district. Subsequently, the POME sample was subjected to vacuum filtration (8.0 μm filter paper). Finally, the filtered POME sample was stored at 277 K.

Catalyst synthesis and characterization

In this study, 20 wt% of Ni metal was wet-impregnated onto Al_2O_3 particle. $Ni(NO_3)_2.6H_2O$, a pre-cursor of Ni metal, was accurately weighed into a beaker and dissolved in 100 mL of deionised water. Subsequently, Al_2O_3 solid which was pre-calcined at 1073 K, was mixed with the Ni salt solution, and the resulting slurry was stirred vigorously for 3 h. This step was followed by drying process which was carried out at 373 K for overnight using a Thermo-Fisher Heraeus Series 6000 oven. The oven-dried solid was then crushed and subjected to air-calcination at 1073 K for 5 h in a Carbolite High-Temperature Box Furnace, employing ramping rate of 10 K min^{-1}. The particle size of catalyst for steam reforming activity evaluation was confined within a range of 140—250 μm using a sieve shaker.

For characterization, the XRD pattern of catalyst was obtained from a Philips X'Pert instrument with X-ray source from CuK$_\alpha$ (λ = 1.542 Å) operating at 45 kV and 40 mA. Crystallite size of the catalyst was computed using the Scherrer equation. Besides, FESEM image was taken using a JEOL FESEM JSM-7100F instrument to capture the surface morphology of as-synthesized catalyst. In addition, the N_2-physisorption was conducted on a Thermo-Scientific Surfer unit at 77 K for textural properties determination. Prior to the test, catalyst was degassed at 573 K at vacuum condition for overnight.

Steam reforming of POME

Steam reforming of POME was conducted in a stainless-steel tubular reactor with an internal diameter of 0.95 cm and a length of 40.0 cm. For each experiment, 0.1 g of catalyst was placed on the quartz wool seated in the middle of the stainless-steel tubular reactor. The reactor was maintained at reaction temperature and blanketed with N_2 carrier gas for 30 min before experiment initiation. During the reaction, POME sample was pumped into the reactor in the presence of N_2 as a diluent gas. The outlet liquid product was directed into an ice-bath condenser, then passed through a drierite bed before collected into Tedlar gas sampling bags. The collected liquid sample was subjected to COD analysis using Hach DRB-200 COD instrument and expressed in terms of COD reduction (%) as in Equation (1).

$$\text{COD reduction}(\%) = \left[\frac{COD_i - COD_f}{COD_i}\right] \times 100 \qquad (1)$$

where COD_i and COD_f refer to the initial and final COD readings of the liquid sample. On the other hand, the gas sample collected was eluted using an Agilent 7890B Gas Chromatography instrument which was equipped with two packed bed columns, *viz.* Supelco Molecular Sieve 13 × (10 ft × 1/8 in OD × 2 mm ID, 60/80 mesh, SS) and Agilent HayeSep DB (30 ft × 1/8 in OD × 2 mm ID, 100/120 mesh, SS), for qualitative and quantitative analysis. He (20 mL/min) was used as a carrier gas, while the oven and detector were operated at 393 K and 423 K, respectively.

Results and discussion

Catalyst characterization

XRD pattern in Fig. 1a reveals high crystallinity of calcined 20 wt % Ni/80 wt%Al_2O_3 catalyst, judging from the sharp and intense peak observed. Based on the analysis, peaks observed at