Different heating techniques for biogas reforming to dimethyl ether

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Introduction

The aim of this study is the production of an environmentally friendly fuel (Dimethyl ether-DME) that uses the biogas produced in the anaerobic digestion (AD) from grass silage liquor as a feedstock. Reforming of biogas to synthesis gas (syngas) is a highly endothermic process. Alternative methods of heating (traditional electrical furnace and a 2kW induction heating (radiofrequency) unit for low and high pressure) are being investigated for less carbon deposition and energy savings.

Experimental

Biogas Production. Batch and continuous mesophilic anaerobic digestion of grass silage liquor was studied. The continuous process was carried out in Armfield digesters.

Biogas Reforming. A sol-gel method[1] was applied to prepare perovskite $Na_{0.5}La_{0.5}Ni_{0.3}Al_{0.7}O_{2.5}$ catalyst. Herein two different reactor configurations have been used for the reforming of biogas in a temperature range 600-900 ˚C.

DME Synthesis. $CuO/ZnO/Al_2O_3$ (CZA)/HZSM-5(80) was used as admixed catalyst for DME production from Syngas. DME synthesis was carried out in an isothermal fixed bed reactor. The pressure of the reactor was controlled by means of back pressure regulator. The activity tests were carried out in a temperature range of 200–260 ˚C, at 20 bar.

Catalyst Charactarizations. XRD, BET, elemental analysis, XPS, DRIFTS and Raman S. were used.

Results and Discussion

Grass silage liquor can produce a high quality methane stream between 70% and 80% and achieve methane yields of 0.385 m^3 kg^{-1} COD as shown in Table (1).

Table 1. Results of armfield digesters

Property	Unit	COD for silage feed (mg/l)		
		8510	14220	17720
OLR	kg COD/m^3/day	0.851	1.422	1.772
HRT	days	10	10	10
COD removal	%	86.1	98.3	97
CH_4	%	77	73	70
CO_2	%	22	22	22
O_2	%	0.8	0.6	0.3
H_2S	ppm	>>[1]	>>[1]	279
H_2	ppm	>>[1]	>>[1]	>>[1]

The catalytic activity of the $Na_{0.5}La_{0.5}Ni_{0.3}Al_{0.7}O_{2.5}$ perovskites remained stable for 6 h on stream and the catalyst is active enough to give the equilibrium conversion at high reaction temperatures with H_2/CO ratio close to 1 as shown in Figure (1).

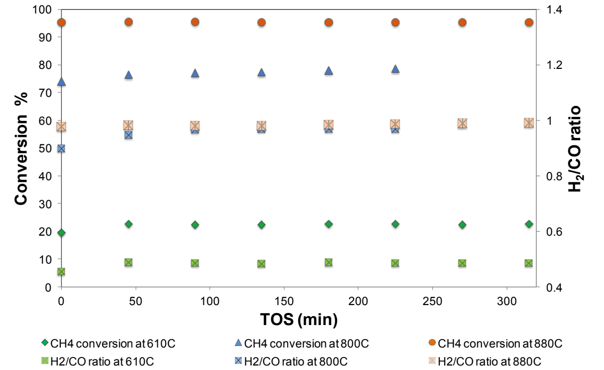

Figure 1. Effect of reaction temperatures on CH_4 conversion for $Na_{0.5}La_{0.5}Ni_{0.3}Al_{0.7}O_{2.5}$ perovskite catalyst.

For the one step DME synthesis a balance must be obtained between the two main catalytic functions. The net acidic function can be modified either through adjusting the acid strength or the quantity of acid sites. The effect of acid fraction in the admixed catalyst has been studied, and as a sequence CZA/HZSM-5 bifunctional catalyst with a 0.25 acid fraction showed high stability over a continuous period of 212 h. sees Figure (2).

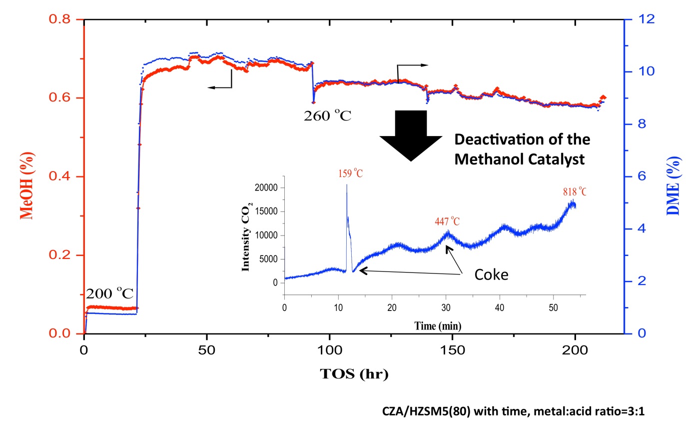

Figure 2. Long term test of DME and MeOH production of the admixed catalyst CZA/HZSM5 (80) with time, metal:acid ratio = 3:1. The catalyst was reduced in 5% H2/He @ 250˚C, catalyst weight: 250 mg, WHSV: 2400 ml g^{-1} h^{-1}.

Conclusions

This work has demonstrated that grass silage liquor can be used to produce a high quality methane stream between 70% and 80% in both batch and continuous reactors. Herein experiments using radiofrequency heating have been performed in order to demonstrate the potential of using rapid heating techniques to convert biogas to a higher heating value syngas. For DME from Syngas, different acid solid catalysts were studied as dehydration component in direct DME synthesis (NH_4ZSM-5 (SiO_2/Al_2O_3 = 23, 80), HZSM-5 (SiO_2/Al_2O_3 = 80) or γ-Al_2O_3). From those tested it was found that the HZSM-5 catalyst has the most stable acid function when considering overall application including long term storage. The effect of acid fraction in the admixed catalyst was also studied. Moreover, the stability of the CZA/ HZSM-5 with a ratio of 3:1 was studied over a continuous period of 212 h (~9 days) the results showed that the selectivity of DME keep constant over all the period.

References

[1] Khalesi, A.; Arandiyan, H. R.; Parvari, M., Production of Syngas by CO2 Reforming on MxLa1-xNi0.3Al0.7O3-d (M = Li, Na, K) Catalysts. *Ind. Eng. Chem. Res.* **2008,** 47, (16), 5892-5898.