Potential utilisation of Indonesia's Natuna natural gas field via methane dry reforming to synthesis gas

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The utilisation of high CO_2 content natural gas, such as that found at Natuna island in Indonesia, using methane dry reforming with carbon dioxide to synthesis gas is demonstrated. Highly active catalysts employed for coke-free, stable dry reforming include alumina-supported nickel, either as-prepared or doped with tungsten oxide or calcium oxide, and the supported group VIII metals. No deactivation was observed for the duration of any of the experiments ($>$70 h), and the methane conversion and product distributions were close to those predicted from thermodynamic equilibrium calculations. It is calculated that the application of dry reforming to the Natuna field alone, combined with known gas-to-liquids (GTL) technology, could provide liquid fuel to Indonesia for almost 18 years.

1. Introduction

At Natuna island, Indonesia [1,2] a vast natural gas reservoir (estimated total gas volume of 222 trillion cubic feet (TCF)) lies beneath the sea, the composition of which is shown in table 1. It is estimated that there is 46 TCF of exploitable hydrocarbons at Natuna; this is almost half the size of Canada's known total reserve (97 TCF) in 1992 [3]. However, the Natuna field also contains large amounts of carbon dioxide. Currently it is proposed to sell the natural gas as LNG after carbon dioxide clean up, consisting of two trains of CO_2 separation facilities: (i) offshore separation (figures 2 and 3) to increase the methane composition to 81% (18% CO_2, 0.5% H_2S and 0.5% N_2), and (ii) after transportation through a sub-sea pipeline, on-shore separation, giving a methane-rich gas suitable for liquefaction (figure 2). The impurities from both the separation stages are then injected by a sub-surface aquifer for underground waste gas disposal, but at an estimated 49% of the total cost of the project.

Studies by Crabtree [4] and Leprince et al. [7] have shown that a pipeline grid or conversion into LNG are not always the most economical solutions for natural gas utilisation, especially when the reserve is small and in remote areas. It is sometimes more attractive and viable to convert the natural gas to liquid fuels or higher hydrocarbons, which can be easily achieved using processes based on synthesis gas, such as Fischer–Tropsch synthesis [8], middle-distillate synthesis [9] or methanol-to-gasoline technology [10]. Synthesis gas is produced from methane by reforming reactions, and in the Natuna case it would be convenient to utilise the carbon dioxide present in the feed for methane dry reforming (1).

Table 1
Dry composition of the Natuna natural gas field [13,14].

	(mol%)
CO_2	71
$CH_4 + C_{2+}$ hydrocarbons	28
H_2S	0.5
N_2	0.5

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H^0_{298} = +247\ \mathrm{kJ\,mol^{-1}} \quad (1)$$

$$CH_4 + \tfrac{1}{2}O_2 \leftrightarrows CO + 2H_2 \quad \Delta H^0_{298} = -38\ \mathrm{kJ\,mol^{-1}} \quad (2)$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad \Delta H^0_{298} = +41\ \mathrm{kJ\,mol^{-1}} \quad (3)$$

This is a highly endothermic reaction, but it is possible to decrease the overall heat input to the process by the addition of oxygen (2), resulting in slightly higher H_2/CO product ratios; this is the current practice in the well established steam reforming process [11]. Catalysts which can be used for methane dry reforming include supported nickel [12–14], the noble metals (e.g., Rh, Ru, Ir) [15–17] or group VI transition metal carbides [18,19]. Of these industry favours nickel due to its relatively low price, high activity and also their long experience with this system. The disadvantage with nickel is that it can also catalyse carbon formation. However, research mainly focusing on the related steam reforming reaction has shown that the extent of carbon formation can be reduced by (i) the addition of excess oxidant [11]; (ii) sulphur passivation using a continuous flow of hydrogen sulphide [20]; and (iii) the addition of dopants, for example alkali and alkaline-earth metal oxides [11].

In this paper we have investigated a range of supported nickel catalysts, both unmodified and modified, and noble metal catalysts for the dry reforming of methane to synthesis gas under feedstocks resembling the Natuna gas field composition. The application of dry reforming to high carbon

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Figure 1. The location of Natuna gas field in Indonesia.

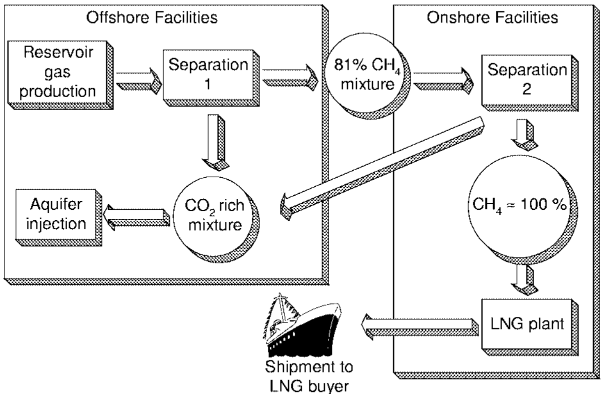


Figure 2. Schematic diagram of the production of Natuna gas for LNG markets [13].

dioxide content natural gas fields is also discussed, and the advantages of this route are presented.

2. Experimental

2.1. Catalyst synthesis

2 wt% Ni/Al_2O_3 (NI2AL) was prepared by wet impregnation with the appropriate amounts of γ-Al_2O_3 (AKZO Chemical Division, high purity, 99.9%, 250–355 μm; surface area $= 224$ $m^2\,g^{-1}$) and $NiCl_2{\cdot}6H_2O$ (BDH Chemical Ltd., 97% purity). The resulting slurry was then dried and calcined in air at 443 K for 15 h and 773 K for 3 h, respectively. The tungsten-oxide-modified alumina-supported nickel catalysts (NI2W0.7AL and NI2W2AL) were prepared by wet impregnating the NI2AL with $(NH_4)_{10}W_{12}O_{41}{\cdot}5H_2O$ (Johnson–Matthey Speciality Products), followed by the same drying and calcination treatment as for the unmodified material. Calcium-modified 8% Ni/MgO (NI8CA2MG) was prepared by first synthesising the unmodified material. This was done by impregnating MgO (Aldrich; 70 $m^2\,g^{-1}$) with $Ni(NO_3)_2{\cdot}6H_2O$ (BDH "AnalaR", 99.0%), and then drying and calcining the resulting slurry at 423 K in air for 15 h and 1073 K in N_2 for 1.5 h, respectively. This material was then impregnated with a calculated amount of $Ca(NO_3)_2{\cdot}4H_2O$ (Aldrich, ACS Reagent 99%), dried at 443 K in air for 15 h and calcined in N_2 at 1073 K for 3 h.

The 5 wt% Ir/Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 (AKZO, high purity; 297 $m^2\,g^{-1}$) with a solution of $(NH_4)_3IrCl_6$. The mixture was dried in air at 373 K for 10 h and calcined in air at 770 K for 22 h. The remainder of the noble metal catalysts were obtained from commercial sources: 5% Pd/Al_2O_3 (PD5AL; Johnson Matthey), 5% Pt/Al_2O_3 (PT5AL; Aldrich), 5% Rh/Al_2O_3 (RH5AL; Koch & Light Laboratories) and 5% Ru/Al_2O_3 (RU5AL; Fluka).

Before reaction all catalysts were dried at 200 °C overnight under N_2, then reduced at 973 K in H_2 for 1 h.

2.2. Catalyst testing and product analysis

The reactor used in this study was constructed from $1/4''$, $1/8''$ and $1/16''$ o.d. 316 stainless-steel tubing and 316 stainless-steel Swagelok fittings throughout. Gas flow rates were controlled using Brooks 5850TR mass flow controllers combined with Brooks 5879 display-controllers, and the gases were then combined and passed to the reactor containing the catalyst. Catalyst samples were placed between two quartz wool plugs in the centre of a 4 mm i.d. silica tube and inserted into a vertical Severn Science tube furnace, heated to the required reaction temperature and controlled from a Eurotherm 905 temperature controller. The exit gas stream was passed to a gas chromatograph for analysis via a heated line to prevent condensation of the products. Experiments were conducted at atmospheric pressure between 773 and 1173 K at a CO_2/CH_4 ratio of $\sim$2.9.

Product analysis was carried out using a Hewlett–Packard 5880A gas chromatograph, fitted with both a thermal conductivity detector, and a methanator/flame ionisation detec-

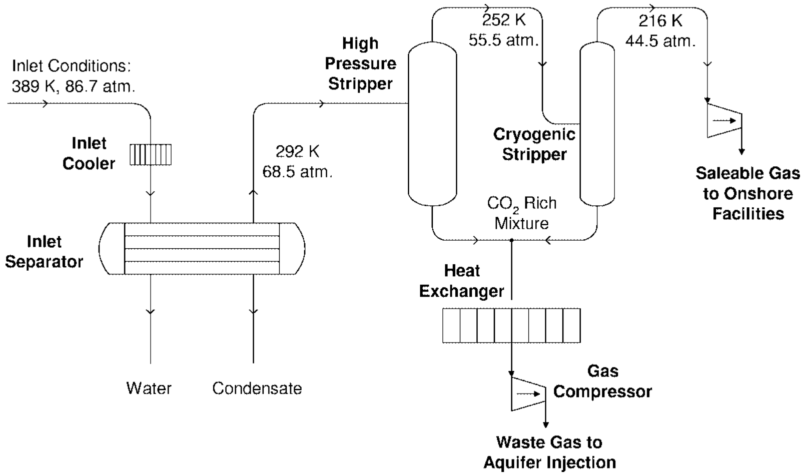


Figure 3. Schematic diagram of CO_2 separation process at treating platform [14].

tor. Separation of the products was achieved using argon carrier gas and 3 m Hayesep R and Porapak T packed columns before the detectors, respectively. Reference data and pure component injections were used to identify the major peaks, and response factors for the products and reactants were determined and taken into account in the calculation of the conversion and product distribution. In all cases carbon balances were better than 97%.

Methane (BOC Ltd., CP Grade, >99.9%), carbon dioxide (BOC Ltd., CP Grade, >99.5%), argon (BOC Ltd., Pureshield grade) and hydrogen (Air Products, >99.99%) were used as received without further purification.

3. Results

3.1. Methane dry reforming over noble metal catalysts using high CO_2 feed excesses

The results obtained using noble metal catalysts together with thermodynamic equilibrium calculations are presented in figure 4. All the product distributions closely follow the thermodynamic equilibrium from 973 K and higher. In the low-temperature region, the relative activity of the catalysts, based on CH_4 conversion followed the order: Ru $\approx$ Rh $>$ Pt $\approx$ Pd $>$ Ir, as mirrored by previous studies under stoichiometric reactant feeds. Figure 4(b) shows the CO_2 conversion values, which deviate from the calculated equilibrium values; this indicates that the reverse-water–gas-shift reaction (RWGSR; equation (3)) is dominating the catalyst performance. The controlling influence of the RWGSR was further borne out by the H_2/CO ratios observed in the experiments and shown in figure 4(c); this ratio was higher than expected from calculations. These observations were also made by Bradford et al. [21], suggesting that the RWGSR is the slowest, and therefore, the rate-determining reaction.

No deactivation was observed over Pd, in contrast with previous studies for the related methane partial oxidation reaction under stoichiometric feedstocks [22]. However, Gadalla et al. suggested that carbon deposition in dry reforming could be avoided in excess CO_2 feeds [23], as is also the case with steam reforming using excess H_2O [11]. The poor performance of the Ir catalyst is probably due to its low activity and not due to carbon deposition, which is unlikely to occur using this feed composition. For the related partial oxidation of methane, even under stoichiometric conditions, it was reported that less than 0.1 mg $g_{cat}^{-1}\,h^{-1}$ carbon deposition was observed on Ru and Ir catalysts [24].

3.2. Methane dry reforming over nickel-based catalysts using high CO_2 feed excesses

NI2AL, NI2W0.7AL, NI2W2AL and NI8CA2MG were tested for methane dry reforming, and the results are shown in figure 5. The CH_4 conversion values (figure 5(a)) reveal that the modified nickel catalysts are slightly less active than Ru and Rh (see figure 4(a)), in accord with previous studies showing that Ru and Rh are the most active metals for methane dry reforming [25]. The results also show that, under the reaction conditions employed here, the performance of the modified and unmodified nickel catalysts was very similar, whereas earlier studies had shown that the WO_3- and CaO-modified catalysts had a higher activity than NI2AL [26]. Figure 5(b) presents the CO_2 conversions obtained from the same set of reactions and shows that thermodynamic equilibrium is not achieved due to the influence of RWGS, as was the case for the noble metal catalysts. This is also demonstrated by the H_2/CO values presented in figure 5(c). These experiments show that the importance of the RWGSR is greatly effected by temperature over both the noble-metal- and nickel-based catalysts, under the reaction conditions used.

It is interesting to note that WO_3 addition appeared to shift the H_2/CO maxima to a higher temperature, indicating that the RWGS reaction is inhibited by the WO_3 addition, while the maxima for the CaO-doped catalyst, although lower than for the other nickel catalysts, was at a higher temperature (985 K) again. The behaviour of the NI8CA2MG catalyst may be attributable to the change in catalyst alkalinity, due to the addition of both an alkaline-earth support

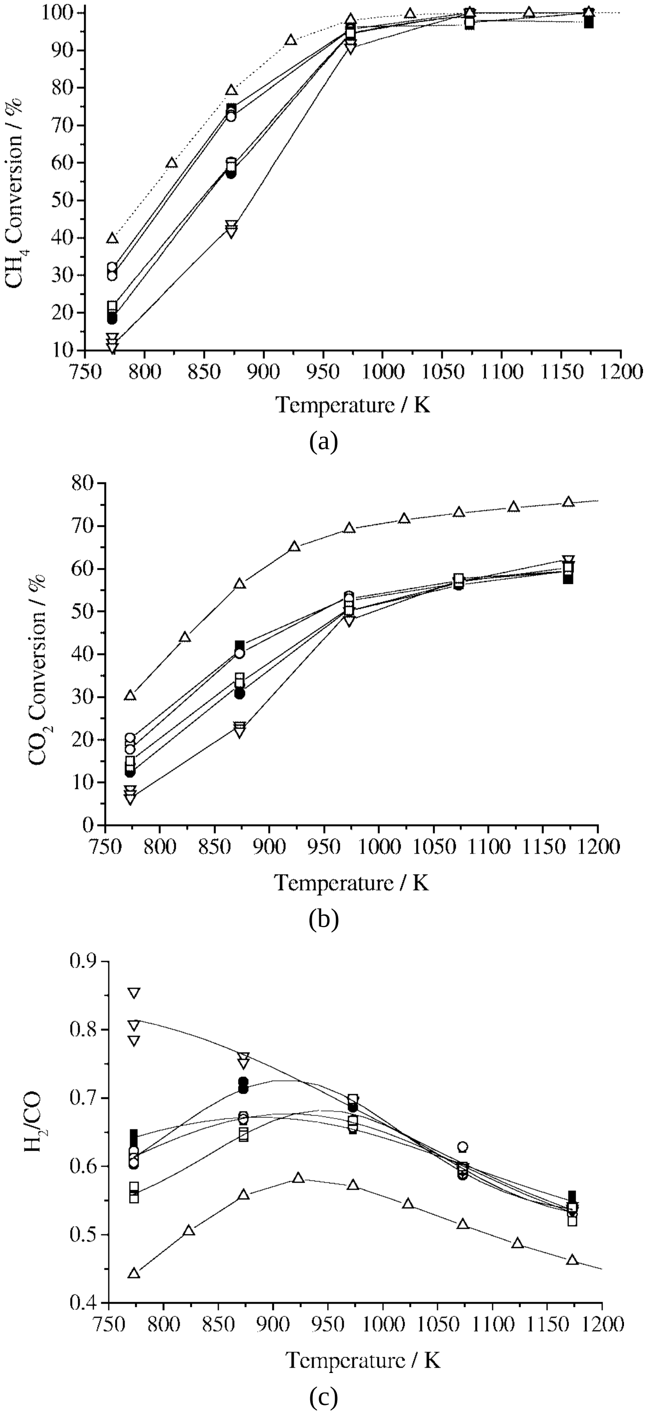


Figure 4. Temperature effect on (a) CH_4 conversion, (b) CO_2 conversion and (c) H_2/CO for methane dry reforming over noble metal catalysts ($CO_2/CH_4 = 2.9$, $p = 1$ atm, 50 mg catalyst); (▽) IR5AL, (•) PD5AL, (□) PT5AL, (■) RH5AL, (○) RU5AL and (△) thermodynamic equilibrium.

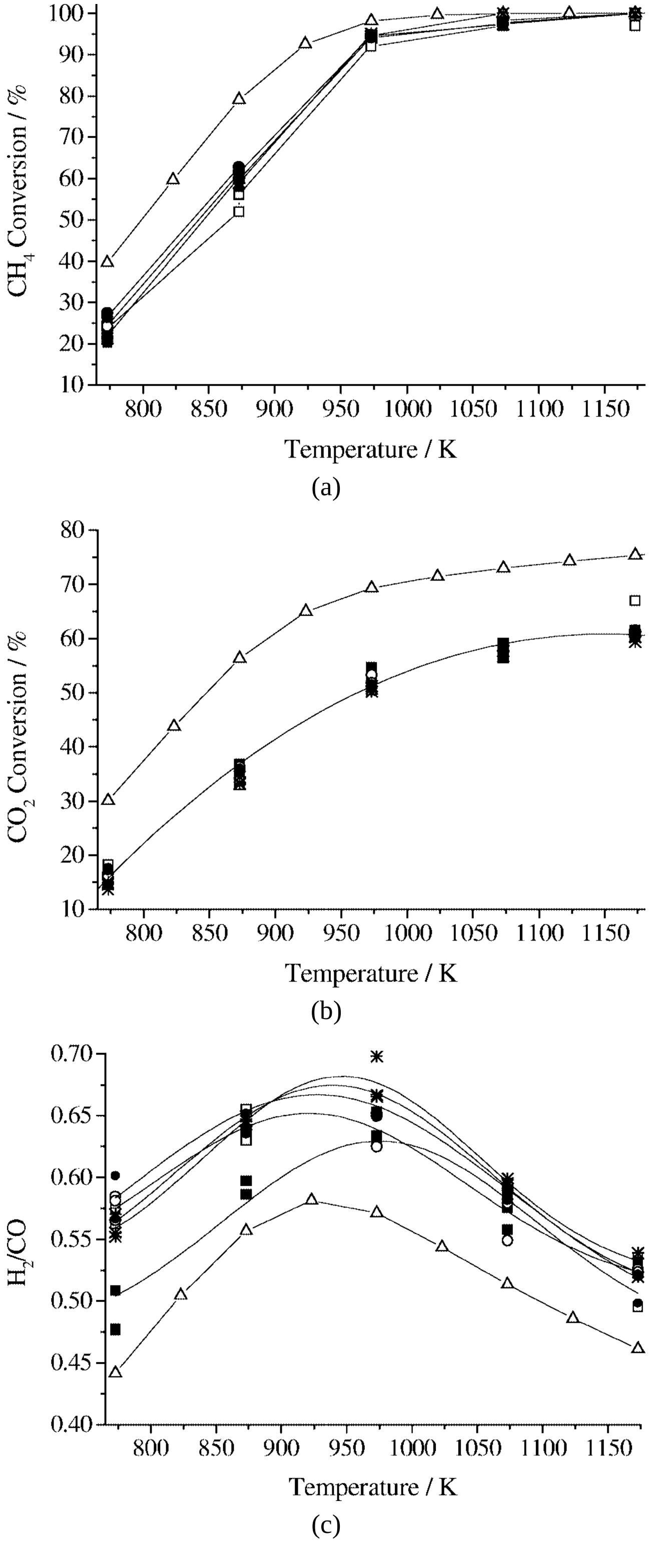
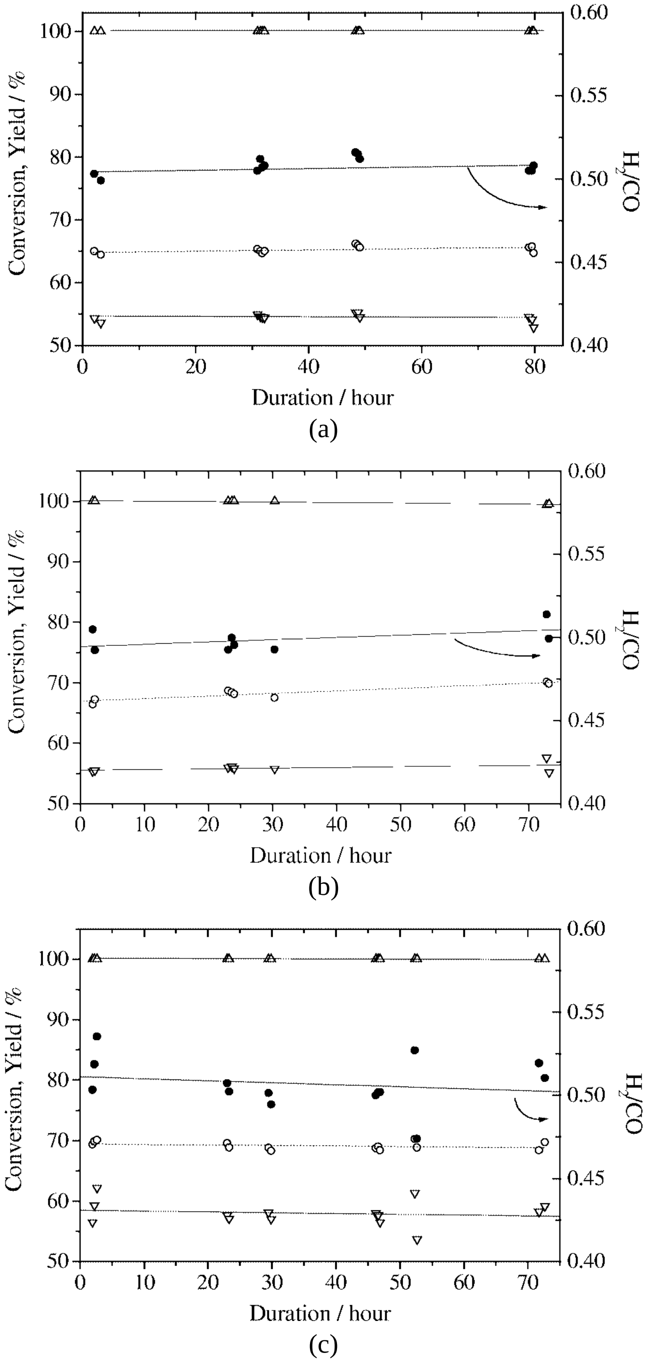


Figure 5. Temperature effect on (a) CH_4 conversion, (b) CO_2 conversion and (c) H_2/CO for methane dry reforming over modified nickel catalysts ($CO_2/CH_4 = 2.9$, $p = 1$ atm, 50 mg catalyst); (○) NI2AL, (•) NI2W0.7AL, (□) NI2W2AL, (■) NI8CA2MG, (∗) PT5AL and (△) thermodynamic equilibrium.

(Mg) and promoter (Ca); this enhanced basicity may retard the RWGSR further relative to the WGSR.

Lifetime experiments were also carried out over NI2AL, NI2W2AL and NI8CA2MG catalysts and the results are shown in figure 6 (a)–(c). No deactivation was apparent over any of the catalysts for the duration of the experiments (<70 h). In addition, the initial CO_2 conversions were 54.5% for NI2AL, 57.6% for NI2W2AL and 61.4% for NI8CA2MG, showing that the performance of the modified catalysts was slightly better, in accord with previous studies [26]. Therefore, the WO_3- or CaO-modified catalysts are



(a)

(b)

(c)

Figure 6. Lifetime experiment for methane dry reforming over (a) NI2AL, (b) NI2W2AL and (c) NI8CA2MG ($CO_2/CH_4 = 2.9$, 1123 K, $p = 1$ atm, 105 mg catalyst); (▽) C_{CO_2}, (△) C_{CH_4}, (○) Y_{CO} and (●) H_2/CO.

not only extremely stable, but are also more active than the undoped nickel catalyst.

4. Discussion

It has been demonstrated in the previous section, that nickel catalysts are an excellent choice for CO_2 reforming using high excess CO_2 in the feed compositions. Carbon deposition appears to have been eliminated under the high CO_2 content reactant feed, and therefore, the possibility of applying CO_2 reforming, in combination with GTL or Fischer–Tropsch technology, in the development of Natuna gas project has been demonstrated. Should this scenario be implemented, the potential advantages over the LNG route would be:

(i) Reduced problem of CO_2 separation and disposal: around 60% of CO_2 and 100% of CH_4 would be converted to synthesis gas using nickel-based catalysts, as exhibited by the experimental results in the previous sections. With this conversion, significantly reduced amounts of CO_2 will be found in the effluent stream, which would therefore be easier to handle.

(ii) No more need for gas pipelines: since the products will be mainly liquids, conventional transportation can be used, instead of expensive LNG tankers. In addition, the liquid products could be transported through pipelines, which are far less expensive than gas pipelines [27].

(iii) Production of liquid fuels or chemicals, which are more environmentally friendly: liquid fuels derived from synthesis gas, are usually low in sulphur, nitrogen or other impurities.

(iv) The products could be marketed to wider buyers, as is the case with crude oil: Baharuddin regards liquid fuels as "a commodity" while gas trade is a "long commitment that expresses the close bond between the (trading) nations" [28].

Disadvantages are the cost for the development and the design of a GTL process, which is likely to be significant.

The conversion of natural gas to liquid fuel on a commercial scale can be found in Malaysia (Bintulu SMDS project) and South Africa (Mossgas project), although smaller demonstration plants can also be found elsewhere [29]. Wender [8] and Senden et al. [9] illustrated that with current gas conversion technology, about 8.2×10^3 CF natural gas could be converted to a barrel of premium transportation fuel. If this number is used to estimate the barrel equivalent of the exploitable hydrocarbons contained in the Natuna gas reserve the result will be around 5.61×10^9 barrels (equivalent to 8.93×10^8 m^3) of transportation fuel. If this amount is extracted at the yearly rate of 5.09×10^7 m^3 (Indonesian oil consumption of 1998) [6], the liquid fuel from the converted gas of the Natuna gas field is capable to supply Indonesian liquid fuel demand for almost 18 years. Therefore, a GTL process, employing CO_2 reforming, offers another option for utilising high CO_2 content natural gas produced from the Natuna gas field.

5. Conclusions

Unmodified and modified supported nickel catalysts, and supported noble metal catalysts have been successfully employed for the coke-free dry reforming of methane to synthesis gas. All the catalysts were highly active and stable under the high CO_2/CH_4 ratios used. Thermodynamic equilibrium for CH_4 conversion was achieved at 973 K, but it is suggested that the RWGS dominates CO_2 conversion, resulting in considerably lower CO_2 conversion compared to its thermodynamic equilibrium value. Finally, very simple calculations of capital cost indicate that a GTL process, employing CO_2 reforming as a synthesis gas source, could be advantageous in the Natuna case.

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