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Combined reforming of chemical looping combustion products: A thermodynamic analysis

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ABSTRACT

Existing energy generation processes emit CO_2 gas that is posing a serious problem of global warming and climate change. Chemical looping combustion (CLC) coupled combined reforming (CR) is an innovative way for clean energy generation and syngas production. A thermodynamic analysis of CR of propane was done using Gibbs free minimization routine of HSC Chemistry 5.1. The product stream of CLC reactor (mainly CO_2 and H_2O) was mixed with additional propane with/without oxygen (air) at 1 bar pressure in the CR reactor and the product & byproduct yields with CO_2 and H_2O conversions was found within the temperature range 450–950 ºC. The objective of the paper is to identify the thermodynamic domain of the process operation, study the variation of product distribution pattern and describe the optimum conditions to maximize the yields of desired products with minimum undesired product formation. It was found that higher CO_2 conversion to syngas would require higher energy from the CLC reactor. Operation of the CR reactor at oxygen to carbon in propane ratio 0.2 above 650 ºC was identified as the best operating point that gave a good balance of CO_2 conversion, enthalpy requirements and syngas generation with zero carbon and low methane formation. These calculations were done for propane fuel and can also be used for other fuels.

KEYWORDS

Combined reforming;
Thermodynamic analysis;
Propane reforming;
CO_2 utilization;
CLC;
CR.

INTRODUCTION

“Fuel Reforming” is a well developed area in chemical engineering field. Reforming mainly refers to the conversion of fuel to a product stream mainly containing syngas along with CO_2, CH_4, H_2O and carbon. Syngas is a useful value added product for many applications. Syngas has been used as raw material to produce hydrocarbons[1,2], as fuel in Internal Combustion (IC) engines[3-6], for synthesis of Liquefied Petroleum Gas (LPG)[7-9], gasoline[10], alcohols[11-16], dimethyl ether[17,18], as fuel in gas turbines[19,20], for use in coal liquefaction[21], for use in co-firing and reburning in a coal fired boiler[22], for synthesis of methanethiol[23], as fuel in fuel cells[24] and also to synthesize biofuels by syngas fermentation[25]. Partial oxidation (PO), steam reforming (SR), autothermal reforming (ATR), dry reforming (DR), dry autothermal reforming (DATR), and chemical looping reforming (CLR) for syngas production are known processes in chemical engineering research. Chemical looping combustion (CLC) is a new process for energy production that uses indirect oxidation of fuel using an oxygen carrier completely to CO_2 and H_2O. The product stream is cooled to separate the condensate water and pure CO_2 stream is compressed and injected deep into oil fields for enhanced oil recovery thus preventing CO_2 pollution to atmosphere. But the safety of this CO_2 sequestration technique and cooling of the CLC product stream to separate CO_2 and water are not the only ways to process the products of CLC. CLC coupled combined reforming (CR) is another way for producing value added products such as syngas[26]. The combined reforming process uses a catalytic reactor that combines steam reforming, dry reforming and partial oxidation reactions to produce syngas rich product stream. Combined reforming is also studied by many researchers. Michael et al.[27] have experimentally studied the PO, SR and DR of methane on Rh/Al_2O_3 catalysts and produced syngas of various ratios in one step process. Maestri et al.[28] have reported microkinetic models for steam and dry reforming of methane on Rh catalysts and concluded that the overall reaction rate is first-order dependant on CH_4 concentration and independent of the co-reactants (H_2O or CO_2). Li et al.[29] have studied the thermodynamic analysis of autothermal steam and CO_2 reforming and reported optimum reformer conditions for coke elimination. York et al.[30] have studied the carbon deposition and deactivation in methane combined reforming (oxyforming). Choudhary et al.[31] have reported reduced $NdCoO_3$ perovskite-type mixed-oxide catalyst (Co dispersed on Nd_2O_3) highly promising material for carbon-free combined reforming of methane to syngas. Song et al.[32] have studied the thermodynamic analysis and experimental testing of combined reforming of methane in a fixed-bed flow reactor and reported over 95% CH_4 conversion and over 80% CO_2 conversion using Ni supported on an oxide substrate catalyst. Le et al.[33] have studied the low temperature plasma combination of steam and dry reforming and reported lower net production of CO_2 and possibility of elimination of CO_2 separation from natural gas for hydrogen generation. Naqvi et al.[34] have presented the idea of producing syngas from CO_2 and steam to avoid carbon plugging of DR reactors. Tomishige et al.[35] have experimentally studied the effect of oxygen addition to steam and dry reforming of methane over Pt and Ni catalysts and reported the effective heat transfer from oxidation to reforming zones for Pt catalysts. Panczyk et al.[36] have reported the improved coking resistance of commercial catalysts modified by small additions of promoters such as K, Ba, Ce, W and Mo compounds in experimental study of CO_2 and steam reforming of n-butane. Qin et al.[37] have experimentally studied the MgO-supported noble metal catalysts for combined reforming and reported lower than equilibrium conversions for CH_4.

A detailed thermodynamic analysis of the product distribution trend of the CR process has not been published in literature yet. Such an analysis is useful to determine the operational conditions of CR reactor to maximize the yields of desired products and minimize the undesired product formation. The process energy requirement can be partially or completely met by the CLC process operation as the combined reformer can operate with and without oxygen (air) addition. Propane (a major component of LPG) was selected as fuel for this study.

THERMODYNAMIC ANALYSIS

Thermodynamic modeling for processes is done by using programs that mostly use Gibbs free energy minimization algorithms[38] or software packages like the equilibrium reactor module of Design II, HYSYS, Aspen Plus or fluent software. HSC Chemistry software version 5.1[39] has been used to generate the data for this study. Thermodynamic equilibrium calculations in the Gibbs routine are done using the Gibbs energy minimization method. The Gibbs program finds the combination of most stable species where the Gibbs energy of the system attains its minimum at a fixed mass balance (a constraint minimization problem), constant pressure and temperature. Hence chemical reaction equations are not required in the input. This procedure of using chemical species instead of simultaneous solution of non-linear reaction equations is found beneficial by many researchers and details about Gibbs free minimization and HSC Chemistry are available in earlier publications[40]. The species such as C_3H_8 (g), O_2 (g), N_2 (g), CO_2 (g), H_2 (g), CO (g), H_2O (g), CH_4 (g), H_2O (l) and C(s) are considered in this study. Ethane (C_2H_6) and other C2, C3 species were considered for the study in preliminary cases. Since negligible formation of these hydrocarbons was observed, it was decided to neglect them in further study. The input species are propane, oxygen, nitrogen, water and CO_2 (all in gaseous phase) reacting to give the products. The material and energy balances are done by HSC Chemistry database and the results may be different using different software. The results presented are within reasonable error limit. Any other inerts in feed, product–byproduct formation is not considered in this study. The steam reforming, dry reforming and partial oxidation reaction chemistry for hydrocarbon fuels is well established in chemical literature and hence no such details are presented in this paper. The products of the CLC fuel reactor will be different for different systems and operating parameters. These are mixed with the additional fuel and oxygen and fed to the CR reactor. The chemical reaction occurring inside a typical CLC fuel reactor (assumed for this study) using propane as fuel and $CaSO_4$ as oxygen carrier is represented as:

R1: $C_3H_8(g) + 2.5CaSO_4 = 2.5CaS(g) + 4H_2O(g) + 3CO_2(g)$

It is assumed that the CLC product stream contains only CO_2 and H_2O in ratio 3:4 and change in oxygen carrier does not alter this ratio as it depends only on the fuel used. 1 mol propane along with 3 moles CO_2 and 4 moles H_2O in feed have been used for all cases. The temperature range of 450 – 950 ºC at 1 bar pressure was used. As steam to carbon ratio (S/C) and CO_2 to carbon in fuel ratio are important parameters in steam and dry reforming processes, similarly variation of feed fuel rate at constant CO_2: H_2O ratio is important factor to study the variation in product distribution of this process, as the combined (CO_2 and H_2O) stream of fixed ratio comes directly from the CLC reactor. Hence variation of input fuel (without oxygen) in CR and variation of oxygen in CR reactor at constant fuel, CO_2 and H_2O inputs were the two important cases identified and process product-enthalpy distribution with reactant conversion trends for these two cases was studied. The variation of feed propane was done by gradually increasing the moles from 0.5 to 1.5 in intervals of 0.5 moles at constant CO_2 and H_2O feeds in the first case (conditions : A, B and C). In the second case, 1 mol propane, 3 mol CO_2 and 4 mol H_2O were kept constant and OCPR (oxygen to carbon in propane ratio) was increased from 0.2 to 1.0 in intervals of 0.2 (conditions: B2, B4, B6, B8 and B10). The effect on product gas yields, reactant conversions and process enthalpy at different temperatures was analyzed and discussed.

RESULTS AND DISCUSSION

The effect of temperature and feed variation in combined reforming of propane on the equilibrium product compositions is analyzed and discussed in this section. The trend with regard to the variation of products was similar for both the cases of change in reactant propane moles and change in OCPR ratio. A detailed analysis along with a graphical representation of the data has been provided in the preceding section. Thermoneutral temperature is an important concept used in the results analysis. Thermoneutral temperature can be understood as that particular temperature at which the reaction enthalpy becomes zero i.e. there is no requirement of external energy (for heating or cooling) to the system. This condition is achieved when the net reaction enthalpy balances the exothermic and endothermic reactions in the process.

Process enthalpy

Reaction enthalpy is a very important entity in chemical processes. Since the product stream of CLC reactor will usually be at higher temperature, the only external heat required for the CR reactor will be mostly consist of the reaction enthalpy of the CR reaction. The reaction enthalpy for combined reforming of propane without oxygen was studied for molar feed values of C_3H_8 varying from 0.5 to 1.5, and the results are shown in figure 1 (A-B-C). It is observed that the process endothermicity increases with increase in temperature and also with increase in C_3H_8 feed rate. The reaction enthalpy for the CR process in the temperature range 450 to 950 ºC increases from 178 to 645 kJ, from 191 to 1000 kJ and from 205 to 1360 kJ for propane feed values of 0.5, 1.0 and 1.5 moles respectively. The reaction enthalpy in combined reforming of propane with oxygen addition was studied for OCPR values varying from 0.2 to 1.0 and the results are plotted in figure 1 (B2-B10). The point at which the enthalpy curve touches the temperature axis is the thermoneutral point. It is observed that the process endothermicity increases with increase in temperature at constant OCPR and the process endothermicity decreases with increase in

OCPR at constant temperature. The reaction enthalpy values range from -1.58 kJ to 771.00 kJ (OCPR=0.2), from -196 kJ to 540 kJ (OCPR=0.4), from -390 kJ to 308 kJ (OCPR=0.6), from -587 kJ to 75.20 kJ (OCPR=0.8) and from -792 to -158 kJ (OCPR=1.0) within the temperature range 450 – 950 ºC for the process. The thermo-neutral temperatures (within 450 – 950 ºC range considered in this study) were observed for OCPR values of 0.4, 0.6 and 0.8 and located at 537.55ºC, 626.73ºC and 873.13ºC respectively.

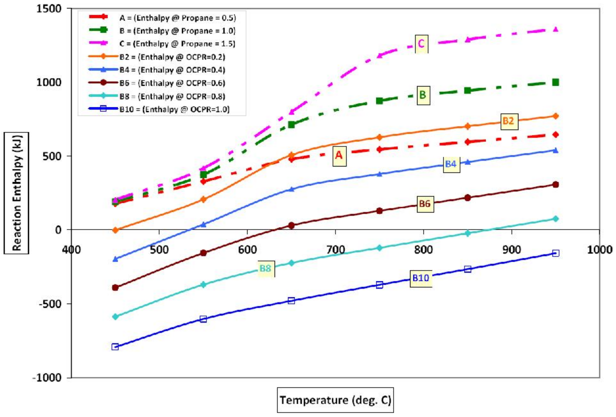

Figure 1 : Reaction enthalpy in combined reforming of propane.

Hydrogen yield

Hydrogen is a valuable product of reforming processes as it has many applications including use in fuel cells and syngas production. The H_2 yield for combined reforming of propane without oxygen input was studied and the results obtained are shown in figure 2 (A-B-C). It was observed that the H_2 yield generally increases, reaches a maximum value and then decreases with increase in CR temperature and the H_2 yield is directly proportional to the moles of C_3H_8 in feed. The maximum hydrogen yield for increase in C_3H_8 feed from 0.5 to 1.5 moles was found to be 3.14, 5.79 and 8.48 moles at temperatures 667.5°C, 748°C and 827°C respectively. However, it was also found that the hydrogen yield per mole propane feed declined from 6.28 (0.5 mol propane) to 5.79 (1 mol propane) and 5.65 (1.5 mol propane). The H_2 yield for combined reforming of propane (constant 1 mol) with gradual increase in oxygen feed is also shown in figure 2 (B2-B10). In this case too, it was observed that the H_2 yield initially increased, reached a maximum value and then decreased with increase in CR temperature and the lower OCPR feed gave higher hydrogen yield (T > 600ºC). The maximum hydrogen yields for increase in OCPR from 0.2 to 1.0 were found to be 5.25, 4.71, 4.16, 3.56 and 2.9 moles at temperatures of 706.5°C, 670.5°C, 636.5°C, 606.5 and 576°C respectively. The hydrogen yields at thermo-neutral temperatures for OCPR values of 0.4, 0.6 and 0.8 were 3.19, 4.15 and 2.82 moles respectively. It is observed that as the OCPR increases, the thermo-neutral temperatures increase, but the H_2 yield first increases and then decreases.

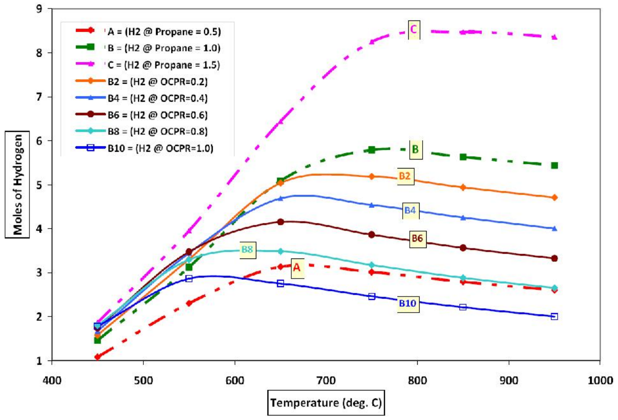

Figure 2 : Hydrogen yield in combined reforming of propane.

CO yield

Carbon monoxide is a desired product for applications that use syngas as raw material and also can be used in some fuel cells like the SOFC, but is strictly a poison for PEMFC although CO can be converted to hydrogen using a series of WGS reactors, preferential oxidation reactor / methanation reactor and then the produced hydrogen stream can be used in PEMFC. The CO yield for combined reforming of propane without oxygen feed for variation in feed of C_3H_8 moles from 0.5 to 1.5 is shown in figure 3 (A-B-C). It was observed that the CO yield generally increases with increase in CR process temperature and it is directly proportional to the feed moles of C_3H_8 at higher temperatures. It was seen that the CO yield was similar for all C_3H_8 molar feed values at lower temperature (<550ºC), but later increased with higher C_3H_8 molar feed values and then increased very slowly at higher temperatures. The maximum CO yields for increase in C_3H_8 feed moles from 0.5 to 1.0 and 1.5 were found to be 2.40 moles, 4.56 moles, 6.63 moles respectively at 950°C, while the corresponding minimum CO yields were found to be 0.133 moles, 0.134 moles, 0.135 moles respectively at 450°C. The CO yield for combined reforming of propane with oxygen is shown in figure 3 (B2-B10). It was observed that the CO yield increased with increase in CR temperature, but it decreased with increase in OCPR at constant temperature. Higher CO yield was favored by lower OCPR and higher temperatures. The maximum CO yields for increase in OCPR were found to be 4.09 moles (for OCPR = 0.2), 3.85 moles (for OCPR = 0.4), 3.08 moles (for OCPR = 0.6), 2.55 moles (for OCPR = 0.8) and 2.00 moles (for OCPR = 1.0) at 950°C, while the minimum CO yields were found to be 0.167 (for OCPR 0.2), 0.183 (for OCPR = 0.4), 0.231 (for OCPR = 0.6), 0.256 (for OCPR = 0.8) and 0.24 (for OCPR = 1.0) at 450°C. The CO yields at thermo-neutral temperatures for OCPR values of 0.4, 0.6 and 0.8 were found to be 0.98, 1.97 and 2.38 moles. Thus as the OCPR increased, the thermo-neutral temperature and the CO yield both increased.

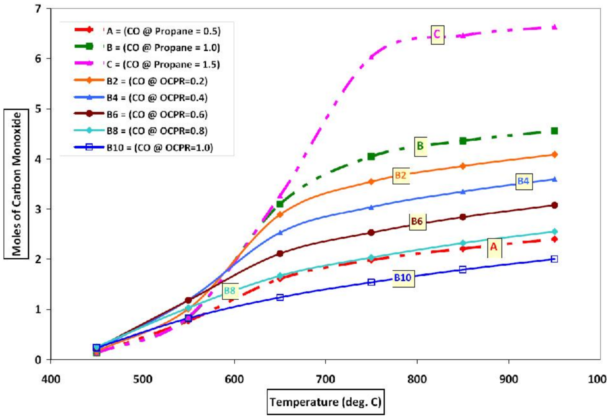

Figure 3 : Carbon monoxide yield in combined reforming of propane.

CO_2 conversion

The main objective of combined reforming process is to utilize CO_2 to produce valuable products such as hydrogen / syngas and sometimes also carbon as CNF (carbon nanofilaments) formation has been reported by some researchers in CO_2 reforming[41,42]. The estimation of CO_2 conversion at various temperatures and feed variations is therefore important. The CO_2 conversion (%) obtained in combined reforming of propane without oxygen input was studied for variation in molar feed values of C_3H_8 from 0.5 to 1.5 and the results were plotted in figure 4 (A-B-C). It was observed that the CO_2 conversion initially decreased with increase in CR temperature (till 550 ºC) but then increased with temperature for all feed molar values of C_3H_8. It is evident from the graph that higher CO_2 conversion is favored by higher C_3H_8 molar values and higher temperatures. The maximum CO_2 conversions obtained for C_3H_8 feed moles of 0.5, 1 and 1.5 were found to be 30.00, 52.00 and 71.07 respectively at 950°C. The CO_2 conversion for combined reforming of propane with oxygen addition was studied for OCPR increase from 0.2 to 1.0 and the results obtained were plotted in figure 4 (B2-B10). The CO_2 conversion initially decreased for OCPR 0.2 and 0.4 but later increased for OCPR 0.6, 0.8 and 1.0, with increase in CR temperature. It is seen from the graph that higher CO_2 conversions are favored by higher temperatures and lower OCPR. The negative value of CO_2 conversion depicts more CO_2 emission from the process. The minimum CO_2 conversion for oxygen addition to the CR process was found to be -75.67% at OCPR 1.0 and 450°C, while the maximum CO_2 conversion was found to be 36.33 at 0.2 OCPR and 950°C. The CO_2 conversion at thermo-neutral temperatures for OCPR values of 0.4, 0.6 and 0.8 were found to be -33.82%, -32.21% and -20.81% suggesting that thermoneutral operation of the process at these points may not contribute to CO_2 sequestration. It was observed that as the OCPR increased the thermo-neutral temperature and the CO_2 conversion both increased.

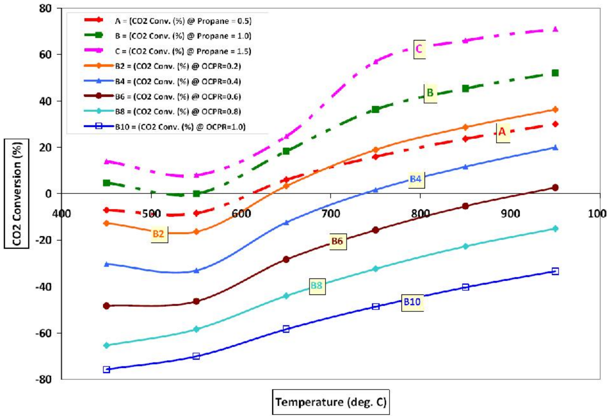

Figure 4 : CO_2 conversion in combined reforming of propane.

CH_4 formation

Methane formation is assumed in all reforming process calculations as it is a very stable hydrocarbon and is mostly present in products of reforming processes. Although methane formation leads to loss of hydrogen and carbon which is undesirable but is not toxic to the downstream operations. The CH_4 yield in combined reforming of propane without oxygen with varying the propane moles in feed (from 0.5 to 1.5 moles) was studied and the results obtained were plotted in figure 5 (A-B-C). It was observed that the CH_4 yield generally decreased with increase in CR temperature and finally became zero for all cases. It was also seen that the lower CH_4 yield was favored by lower propane feeds and higher temperatures. The methane yield decreased from 1.72 moles (450ºC) to zero moles (950ºC); from 1.20 moles (450ºC) to zero moles (850ºC) and from 0.74 moles to zero moles (750ºC) for the propane feed moles of 1.5, 1.0 and 0.5 moles respectively. The CH_4 yield for variation in OCPR at constant propane, CO_2 and water inputs to the CR reactor was studied and the results are shown in figure 5 (B2-B10). It was observed that the methane formation was favored at lower temperatures and lower OCPR. The methane yields for all OCPR values finally decreased to zero value at higher temperatures. The maximum CH_4 yields were found to be 1.07 (OCPR = 0.2), 0.98 (OCPR = 0.4), 0.90 (OCPR = 0.6), 0.79 (OCPR = 0.8), 0.49 (OCPR = 1.0) at 450ºC. It was also observed that as the OCPR increased, the temperatures for getting zero methane yields decreased. The CH_4 yields at thermo-neutral temperatures for OCPR values of 0.4, 0.6 and 0.8 were found to be 0.71, 0.07 and 0.00 moles. Thus it was observed that as the OCPR increased, the thermo-neutral temperature increased and the CH_4 yield decreased.

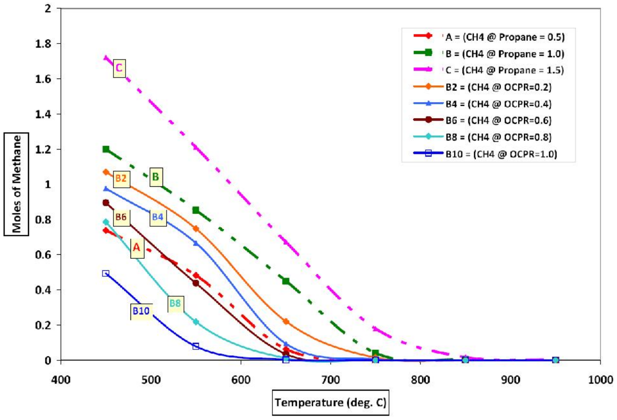

Figure 5 : Methane yield in combined reforming of propane.

Syngas (H_2+CO) yield

The syngas (H_2+CO) yield is the most important component of this thermodynamic study. Syngas is the most useful product of reforming processes and has multiple applications. The syngas yield in combined reforming of propane without oxygen addition was studied for variation in molar feed values of C_3H_8 from 0.5 to 1.5 and the results obtained were shown in figure 6 (A-B-C). It was observed that the syngas yield increased with increase in CR temperature till a certain temperature and then remained almost constant. The syngas yield increased with increase in propane feed. It was seen that the syngas yield increases from 1.21(450ºC) to 4.99 (750ºC), increases from 1.59 (450ºC) to 9.99 (850ºC) and increases from 2.00 to 14.99 (950ºC) for propane feeds of 0.5, 1.0 and 1.5 moles respectively. The results of the syngas yield in combined reforming of propane for increase in oxygen input are shown in figure 6 (B2-B10). The syngas yield generally showed decline with increase in OCPR. It was seen from the graph that higher syngas yield was favoured by higher temperatures and lower OCPR. The maximum syngas yields were found to be 8.80 (OCPR = 0.2, T > 850ºC), 7.60 (OCPR =0.4, T > 750ºC), 6.40 (OCPR = 0.6, T > 750ºC), 5.20 (OCPR = 0.8, T > 750ºC) and 4.00 (OCPR = 1.0, T > 650ºC). The syngas moles obtained in the temperature range of 450 – 950 ºC ranged from 1.75 to 8.80, 1.87 to 7.60, 1.97 to 6.40, 2.06 to 5.20 and 2.02 to 4.00 for OCPR increase from 0.2 to 1.0 showing a decrease in range with increase in temperature and OCPR. The syngas yields at thermo-neutral temperatures for OCPR values of 0.4, 0.6 and 0.8 were found to be 4.17, 6.11 and 5.20 moles respectively. It was seen that as the OCPR increased, the thermo-neutral temperature increased and the syngas yield first increased and then decreased.

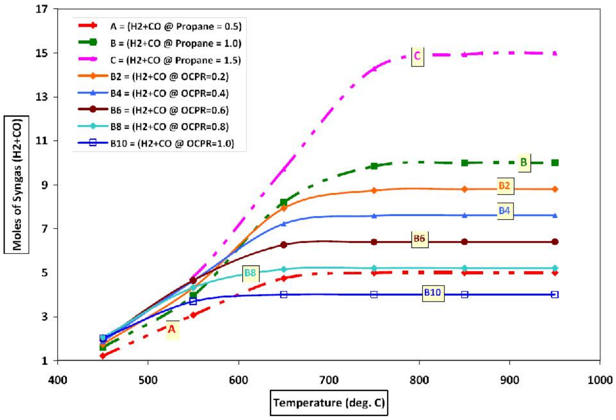

Figure 6 : Syngas yield in combined reforming of propane.

Syngas ratio (H_2/CO)

Syngas ratio is an important factor for petrochemical manufacture by FT synthesis and the desirable syngas ratio range is 0 to 2. The variation of product syngas ratio in combined reforming of propane for increase in molar feed of C_3H_8 from 0.5 to 1.5 without oxygen input was studied and the results obtained were plotted in figure 7 (A-B-C). It was observed that the syngas ratio decreased with increase in CR temperature for all cases. The initial decrease in the syngas ratio was very steep between 450 – 550ºC, i.e. 8.12 to 2.99, 10.90 to 3.75 and 13.78 to 1.26 but later the decrease was slow to final values of 1.08, 1.19 and 1.26 at 950ºC for propane feeds of 0.5, 1.0 and 1.5 moles respectively. It was also seen that higher propane in feed showed higher syngas ratio values. Thus lower syngas ratio was favored by lower C_3H_8 feed and at high temperatures. The variation of product syngas ratio in combined reforming of propane with increase in oxygen to feed was studied and the results were plotted in figure 7 (B2-B10). It is observed that the syngas ratio decreased rapidly at lower temperatures (450 – 550ºC) and then slowly decreased at higher temperatures. Thus a lower syngas ratio was favoured by higher temperatures and higher OCPR. The syngas ratios in the range of 4.00 to 1.00 are obtained in the temperature range 550 – 950ºC. The maximum syngas ratio values observed at 450ºC showed a decrease with increase in OCPR, i.e. 9.46 (OCPR=0.2), 8.39 (OCPR=0.4), 7.53 (OCPR=0.6) till 7.03 (OCPR=0.8) before increasing to 7.45 (OCPR=1.0). The syngas ratio values obtained at thermo-neutral temperatures for OCPR values of 0.4, 0.6 and 0.8 were found to be 3.25, 2.11 and 1.19 respectively. It was observed that as the OCPR increased, the thermo-neutral temperature increased and the syngas ratio decreased.

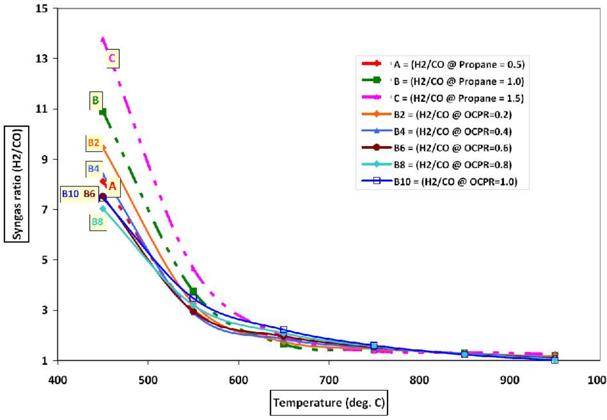

Figure 7 : Syngas ratio in combined reforming of propane.

Carbon formation

Usually carbon is also an undesired product of reforming processes; however carbon formation in the form of CNF (carbon nano filament) has been proved valuable in some dry reforming studies. Hence estimation of carbon yield for variations in feed and temperature was also studied. The results obtained for variation of carbon yield at different propane feeds in combined reforming is shown in figure 8 (A-B-C). It was observed that higher propane feed resulted in higher carbon formation and the carbon formation decreased to zero at higher temperatures. The carbon yield decreased from 0.42 (450ºC) to zero (550 – 950ºC), 1.81(450ºC) to zero (650 – 950ºC) and 3.07 (450ºC) to zero (750ºC – 950ºC) for propane feed values of 0.5, 1.0 and 1.5 moles respectively. The carbon yield in combined reforming of propane with increase in oxygen addition was studied and the results were plotted in figure 8 (B2-B10). It was seen that lower carbon yield was favoured by higher temperatures and higher OCPR. The carbon yields obtained at various OCPRs decreased from 1.38 (450ºC) to zero (650 – 950ºC), 0.91 (450ºC) to zero (650 – 950ºC) and 0.42 (450ºC) to zero (550 – 950ºC) for OCPR values of 0.2, 0.4 and 0.6 respectively. No carbon formation in the temperature range of 450 – 950ºC was observed at OCPR values of 0.8 and 1.0. The carbon yields obtained at thermo-neutral temperatures for OCPR values of 0.4, 0.6 and 0.8 were found to be 0.29, 0.00 and 0.00. It was seen that as the OCPR

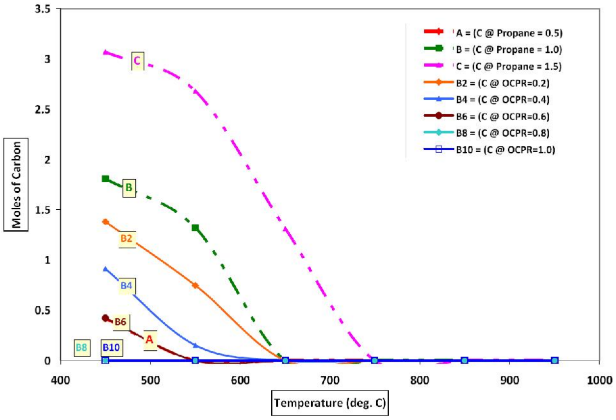

Figure 8 : Carbon formation in combined reforming of propane.

increased, the thermo-neutral temperature increased and the carbon formation decreased.

H_2O conversion

Water is one of the feed components of combined reforming process. In combined reforming maximizing CO_2 conversion is essential, but water conversion can also lead to maximize syngas yield. Water formation is also imminent in reforming processes. Hence process conditions for maximizing water conversion and minimizing water formation in such processes are also important study points. The H_2O conversion in combined reforming of propane was studied for molar feed values of C_3H_8 varying from 0.5 to 1.5, without oxygen and the results were plotted in figure 9 (A-B-C). It was observed that the water conversion initially increased, reached a maximum value and then decreased with increase in CR temperature and higher propane feed required higher CR temperatures yielding higher water conversion at those temperatures. Some negative water conversion data points are also observed at lower CR temperature indicating more water formation in the CR process at those points, however positive water conversion is observed above 525ºC for all cases. The H_2O conversion for combined reforming of propane with oxygen addition at various OCPR values was plotted in figure 9 (B2-B10). The H_2O conversion plot showed the similar variation as seen in case without oxygen addition but with much lower conversion values for all OCPR cases. It was seen from the graph that higher H_2O conversions are favored at middle temperatures (500 – 700ºC) and lower OCPR conditions. The water conversion values obtained at thermo-neutral temperatures for OCPR values of 0.4, 0.6 and 0.8 were found to be 15.28, 7.25 and -29.39. Hence it was observed that as the OCPR increased, the thermo-neutral temperature increased but the water conversion decreased.

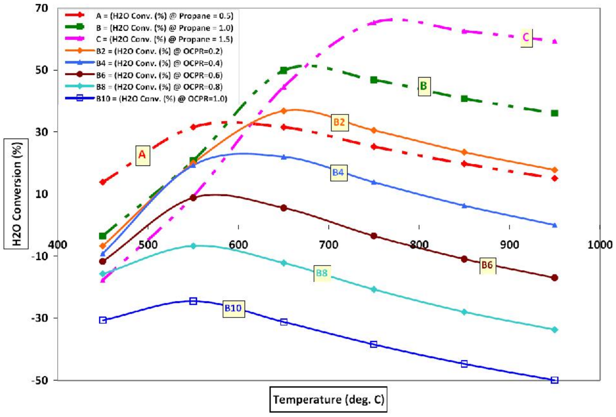

Figure 9 : H_2O conversion in combined reforming of propane.

CONCLUSIONS

The thermodynamic feasibility of using CLC product stream for syngas production via combined reforming process is studied in this paper. The trends of product formation for products such as H_2, CO, CH_4 and carbon along with CO_2 and H_2O conversion and reaction enthalpy at different temperatures, for varying feed propane to CO_2 & H_2O ratio and for gradual oxygen addition to the CR reactor was studied in detail. In combined reforming CO_2 conversion is very important and it decreased with increase in OCPR. Hence, lower OCPR and higher temperature seemed optimum for CO_2 conversion from the CLC stream. Lower OCPR would need additional heat from CLC process. This might be permissible as the net heat from CLC process is huge. Positive CO_2 conversion is observed at C (all cases), B (above 550ºC), A (above 650ºC), B2 (above 650ºC), B4 (above 750ºC), B6 (above 925ºC), while the enthalpy requirements for the process operating above 650ºC are low in the order B6 > B4 > A > B2 > B > C. The moles of syngas generated above 650ºC followed the pattern A < B6 < B4 < B2 < B < C. It was concluded that higher CO_2 conversion to syngas would require higher energy from the CLC reactor. Operation of the CR reactor with OCPR 0.2 above 650ºC was found to be the best operating point from view of balanced CO_2 conversion – enthalpy requirements – syngas generation with zero carbon and low methane formation. The combined reforming process takes care of the hot CO_2 obtained in CLC to generate syngas, thus solving the expensive CO_2 sequestration issue. Experimental results will further reaffirm the process capability.

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