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Thermoneutral point analysis of ethanol dry autothermal reforming

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ABSTRACT

Dry autothermal reforming of ethanol can be used to produce a variety of value added products like hydrogen, syngas and also carbon (possible CNF). A thermodynamic analysis of dry autothermal reforming of ethanol has been carried out to locate the thermoneutral temperatures and product composition at those points at 1, 3, 6 and 9 bar reaction pressures. The variations of thermoneutral temperatures and individual product yields at those temperatures have been discussed to find the optimum operating parameters for desired product output from the process. The process operated at thermoneutral conditions can give useful products like hydrogen, syngas (of low ratio) and carbon (possibly CNFs) and also provide a way for CO_2 sequestration using renewable ethanol fuel. A maximum of 2.58 moles of syngas of ratio 2.01 obtained at 1 bar, CER = 1 and OER = 0.5 along with 0.82 moles of carbon, 0.20 moles of CH_4 and 0.89 moles of water for the thermoneutral temperature of 603.55 °C was found to be the best operating thermoneutral point for value added product generation from this process. This study can be applied to a variety of fuels for producing value added products.

1. Introduction

Climate change has become a crucial issue due to the huge CO_2 emissions to environment. World leaders are united to cut CO_2 emissions. CO_2 sequestration has become an urgent need. Carbon credits are being offered to encourage less pollution and efforts to combat greenhouse gas emissions have already generated a considerable interest worldwide. New methods for CO_2 capture, storage and sequestration are extensively researched worldwide [1,2]. A popular method for CO_2 sequestration is compressing and injecting the CO_2 deep inside earth's crust [3]. However, the questions related to the cost effectiveness and safety of this method are still not answered satisfactorily [4]. Use of CO_2 to produce carbon nanofilaments (CNF) [5,6] or petrochemicals via FT (Fisher Tropsch) synthesis seems to be a viable solution at this moment. Petrochemicals require syngas ($H_2 + CO$) that is presently produced using partial oxidation or steam reforming of fossil fuels like natural gas. But the increase in demand of fossil fuels is pushing the oil and gas prices beyond limits. One example is the huge increase in global price of crude oil (140$/barrel) in 2008. This has prompted the petrochemical industry to find a fresh feedstock for syngas manufacture [7–9]. The spurt of renewable energy has brought biofuels like ethanol, glycerol and biodiesel into limelight. Biofuels are considered as reliable energy sources for the future. Bioethanol, glycerol, etc can be produced in abundant quantities all around the world once the biofuel revolution commercializes. Ethanol is easy to produce, safe to handle, transport and store. Ethanol does not contain heteroatoms (N, S, etc) or metals, and using it in process will not emit NO*x* or SO*x*. CO_2 is another carbon source found abundantly in atmosphere. All flue gases contain CO_2. Plants utilize CO_2 to convert them to carbohydrates. But industrial revolution has resulted in loss of vegetation and an increased CO_2 output to the atmosphere. Although commercial biodiesel manufacture is being done recently, ethanol manufacture from molasses has been well known in industry. Ethanol is a reliable and preferred feedstock and can be used to generate hydrogen and syngas instead of traditional feeds like coal, oil or gas as their reserves have been depleting over the time [10]. Ethanol to syngas by partial oxidation, steam reforming, autothermal reforming and dry reforming has been studied by many researchers. Some important ethanol to hydrogen work reported in literature is summarized below:

1.1. Thermodynamic studies on steam reforming of ethanol

Vasudeva et al. [11] have investigated the thermodynamic feasibility of ethanol steam reforming under conditions conducive to carbon formation and have reported that 5.5 moles of hydrogen can be obtained as against the stoichiometric value of 6.0 per mole ethanol feed. Garcia et al. [12] have conducted thermodynamic analysis of steam reforming of ethanol to produce hydrogen between 1–9 atm, 400–800 K and 0:1–10:1 water to ethanol feed ratio and found that atmospheric pressure and water in excess in the feed gave the best condition for hydrogen production at $T > 650$ K minimizing methane production preventing carbon for-

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mation. Fishtik et al. [13] have studied the thermodynamics of ethanol steam reforming using an algorithm for deriving a unique set of response reactions (RERs) that can be used to rationalize the effect of process variables on steam reforming of ethanol to produce hydrogen and have reported that at or above 700–800 K, and using high water/ethanol ratios, the desired reaction of ethanol steam reforming can be made predominant minimizing the effect of undesirable side reactions. Comas et al. [14] have studied the thermodynamic analysis of ethanol steam reforming using CaO as a CO_2 sorbent and reported that atmospheric pressure, 700 °C and water/ethanol molar ratio of 4 were the best conditions for hydrogen production in the presence of CaO. De Souza et al. [15] have studied the physical–chemical, thermodynamic and exergetic analysis of a steam reformer of ethanol to produce hydrogen and reported that the best thermodynamic conditions for steam reforming of ethanol are the same conditions suggested in the physical–chemical analysis. Da Silva et al. [16] have presented a thermodynamic analysis of ethanol steam reforming to identify conditions for carbon formation and also stated that the work could provide explanations for deviations between thermodynamic analysis and experimental results regarding carbon deposition. Ni et al. [17] have presented a review on reforming bio-ethanol for hydrogen production. Haryanto et al. [18] have presented a review of hydrogen production techniques by steam reforming of ethanol.

1.2. *Kinetics and process engineering aspect studies*

Vaidya et al. [19] have discussed the process engineering aspects of ethanol steam reforming along with catalysts, optimum conditions and ways to prevent problems like coking and byproduct formation. Sahoo et al. [20] have experimentally investigated the kinetics of ethanol steam reforming using Co/Al_2O_3 catalysts in a fixed bed tubular reactor and proposed a kinetic model to describe the steam reforming of ethanol process adequately for a wide range of experimental data. Vaidya et al. [21] studied the catalytic steam reforming of ethanol over a Ru/Al_2O_3 catalyst in 873–973 K temperature range. Mathure et al. [22] have experimentally studied the kinetics of ethanol steam reforming over a commercial nickel–magnesia–alumina ($Ni/MgO/Al_2O_3$) catalyst in a fixed-bed reactor.

1.3. *Oxidative steam reforming/autothermal reforming of ethanol*

1.3.1. *Thermodynamic studies*

Liu et al. [23] have conducted thermodynamic analysis of hydrogen production in oxidative steam reforming of ethanol to calculate the thermoneutral product gas equilibrium moles at 700, 900 and 1100 K and reported that maximum hydrogen with minimum coke and methane were formed at 900 K.

1.3.2. *Experimental studies*

Biswas et al. [24] have experimentally compared steam reforming and autothermal reforming of ethanol over $Ni–CeO_2–ZrO_2$ catalyst and reported that the hydrogen yield was higher in ATR at 500 °C but at higher temperatures higher hydrogen yields were obtained in absence of oxygen. Chen et al. [25] have experimentally studied the autothermal reforming of ethanol using noble metal (Ir, Ru, Rh, and Pd) catalysts supported on various oxides like gamma-Al_2O_3, CeO_2, ZrO_2 and La_2O_3 and found that La_2O_3 was the best support for the ATR reaction and Ir/La_2O_3 gave excellent hydrogen selectivity with good stability on stream and high conversion approaching thermodynamic limit. Cai et al. [26] have studied the ethanol autothermal reforming over an Rh/CeO_2 catalyst and reported that the catalysts exhibited stable activity and selectivity for long term operation without deactivation or sintering. Deluga et al. [27] have also studied ethanol autothermal reforming on rhodium–ceria catalysts and reported that the process has great potential for low-cost H_2 generation applications. Markova et al. [28] have experimentally studied bio-ethanol autothermal reforming to generate data for regression models to provide optimum values of the process factors to maximize hydrogen. Youn et al. [29] have investigated the effect of addition of second metal (Ce, Co, Cu, Mg and Zn) to Ni/gamma-Al_2O_3 catalysts for autothermal reforming of ethanol and found that Cu was the most efficient promoter for hydrogen production. De Lima et al. [30] have tested the catalytic performance of a $Pt/CeZrO_2$ catalyst for ethanol decomposition, steam reforming, partial oxidation, and oxidative steam reforming and proposed a reaction mechanism based on results obtained under reaction conditions. Cai et al. [31] have experimentally tested the oxidative steam reforming of ethanol over an Ir/CeO_2 catalyst and reported complete conversion of ethanol at 773 K with hydrogen, carbon oxides and methane as only products and stable performance of Ir/CeO_2 without deactivation or coking.

1.4. *Dry reforming of ethanol*

Jankhah et al. [32] have studied the thermodynamic equilibrium analysis and experimentation of thermal and catalytic ethanol cracking and dry reforming using a carbon steel catalyst precursor and reported that highest hydrogen and carbon (carbon nanofilaments)) yields were obtained at 550 °C. Wang et al. [33] have studied the thermodynamics of ethanol reforming with carbon dioxide for hydrogen production and have reported that optimum conditions gave over 94% yield of syngas with complete conversion of ethanol without carbon deposition. De Oliveira-Vigier et al. [34] have experimentally studied the dry reforming of ethanol using a recyclable and long lasting SS 316 catalyst and have obtained hydrogen yield 98% of the theoretical value. Blanchard et al. [6] have experimentally studied the ethanol dry reforming using a carbon steel catalyst to produce syngas and also nanocarbons.

No study of ethanol dry reforming with oxygen addition [dry autothermal reforming (DATR) of ethanol] has been reported yet although a similar study for glycerol has been reported [35] which has stated the advantages of DATR over the DR process and role of CO_2 in the process. CO_2 utilization from the CLC (chemical looping combustion) product stream by combined reforming of propane has been recently reported [36].

Autothermal reforming processes are considered more energy efficient due to the in situ energy generation for the endothermic reactions. Dry autothermal reforming is a combination of (endothermic) dry reforming and (exothermic) partial oxidation to produce a syngas rich stream without external energy supply. Thermoneutral point is the condition where the endothermic reactions balance the exothermic reactions to make the net enthalpy of reaction zero. Autothermal processes are generally operated at thermoneutral conditions to maximize energy efficiency. However, very little literature is available regarding thermoneutral points and product trends at those points. Ahmed et al. [37] have theoretically explained the advantages of thermoneutral points of reforming reactions. The main goal of this work is to analyze the thermoneutral conditions for DATR of ethanol process to produce a variety of value added products like hydrogen, syngas and CNF's whose yield can be maximized at different operating conditions and input ratios. This paper intends to study the variation of components in the product stream at thermoneutral conditions, presenting product yields and product distribution trends at various pressures to find the best operating thermoneutral point for the desired product.

2. Methodology

Thermodynamic analysis is the first step for determining the feasibility of clean energy process like DATR of ethanol. Gibbs

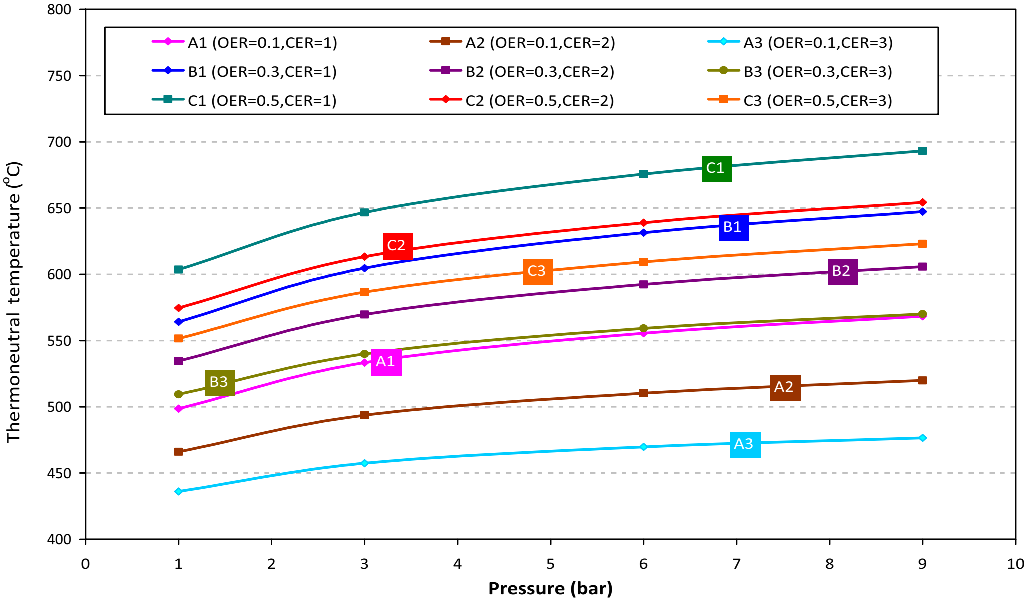

Fig. 1. Thermoneutral temperatures in DATR of ethanol.

free minimization algorithm is commonly used for this step. Various chemical engineering software packages like Design II, HYSYS, Aspen Plus, etc. have equilibrium reactor modules and some of them use the Gibbs free energy minimization algorithms. HSC Chemistry software package [38] (version 5.1) has been used to generate the equilibrium data for this study. The input and desired output species need to be defined by the user along with temperature and pressure conditions. The input species fed to the software were ethanol (both gaseous and liquid state), air (g) and CO_2 (g). The output species fed to the software are H_2, CO, CO_2, CH_4 (all in gaseous state), H_2O (both gas and liquid state) and C (solid), which are common reaction products of reforming reactions. The software gives the individual product moles, along with overall reaction enthalpy at the T and P condition. Temperature, pressure, CER (feed CO_2 to ethanol ratio) and OER (feed O_2 to ethanol ratio) are the key parameters for the process design. The OER is the equivalent of the equivalence ratio, which is defined by the fuel to oxygen ratio compared to the stoichiometric value by some researchers. It was decided to study the process operation at thermoneutral points only, so the data generation is limited to product compositions at thermoneutral conditions for change in CER, OER and pressure. Thermoneutral point temperatures can be obtained from the temperature vs reaction enthalpy graph as it is the temperature at which the enthalpy curve touches the temperature axis where the enthalpy is zero. 1 mole of ethanol has been used at all conditions for this study. The thermodynamic analysis of ethanol dry autothermal reforming has been carried out in the temperature range (450–950 °C) at 1, 3, 6 and 9 bar reaction pressures with CER (feed CO_2 to ethanol ratio) 1, 2, 3 and OER (feed O_2 to ethanol ratio) 0.1, 0.3, 0.5. These conditions represent a realistic view for process operation and are carefully chosen to limit the thermoneutral point temperature to <700 °C which is practical for ethanol feed and also to produce significant carbon (possible CNFs) as they have been reported as useful products by some researchers. The data for variation in yields of products like H_2, CO, CH_4, H_2O and C and also CO_2 conversion at zero enthalpy (thermoneutral) temperatures at different pressures have been generated, analyzed and discussed in the proceeding section. Complete conversion of ethanol and oxygen was found in all cases.

3. Results and discussion

3.1. Thermoneutral points for DATR of ethanol

Thermoneutral point (TNP) is the temperature at which zero net enthalpy is obtained in the autothermal process. It is considered as the best point for autothermal process operation. Lower TNPs are generally preferred to reduce heat losses. Fig. 1 depicts the variation of TNP in DATR of ethanol with change in pressure, CER and OER. As seen from Fig. 1, the TNP increases with increase in pressure at constant CER and OER and also increases with increase in OER at constant pressure and constant CER. However, the TNP decreases with increase in CER at constant pressure and constant OER. At constant pressure, the TNP shows an increase with a simultaneous increase in CER and OER, but it decreases with increase in CER and decrease in OER at constant pressure. Simultaneous increase in pressure, CER and OER generally increases the TNP except for one (P = 6 bar, CER = 1, OER = 0.3 and P = 9 bar, CER = 3, OER = 0.5) point. The TNP range obtained for increase in pressure from 1 bar to 9 bar, was from 436.05 °C to 603.55 °C (P = 1 bar), from 457.38 °C to 646.66 °C (P = 3 bar), from 469.74 °C to 675.61 °C (P = 6 bar) and from 476.47 °C to 693.15 °C (P = 9 bar) at different CERs and OERs. The TNP range obtained for increase in CER from 1 to 3, was from 498.61 °C to 693.15 °C (CER = 1), from 466.08 °C to 654.36 °C (CER = 2) and from 436.05 °C to 623.00 °C (CER = 3) for the considered pressure and OER range. The TNP range obtained for increase in OER from 0.1 to 0.5, was from 436.05 °C to 568.32 °C (OER = 0.1), from 509.37 °C to 647.37 °C (OER = 0.3) and from 551.51 °C to 693.15 °C (OER = 0.5) for the considered pressure and CER range. The minimum TNP for every pressure were obtained at CER = 3 and OER = 0.1 while the maximum TNPs were obtained at CER = 1 and OER = 0.5. Considering all the data points, the minimum TNP of 436.05 °C was obtained at 1 bar pressure, CER = 3 and OER = 0.1 and the maximum TNP of 693.15 °C was found at 9 bar pressure, CER = 1 and OER = 0.5.

3.2. Hydrogen yield at TNP

Hydrogen generation is one of the most desired applications of reforming processes. Thermoneutral operation of the process

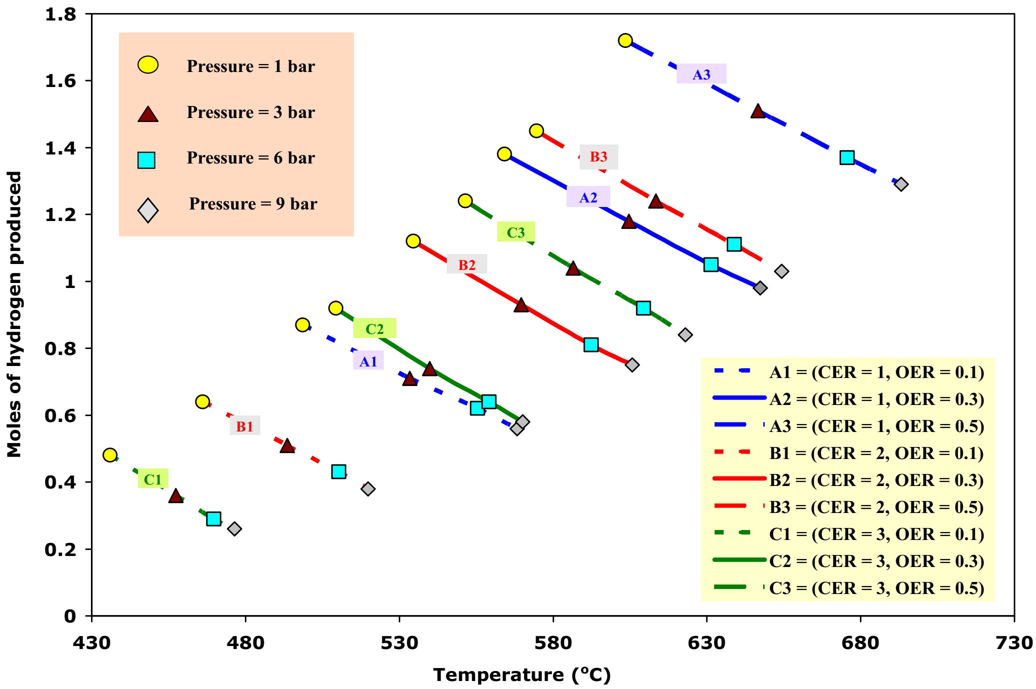

Fig. 2. Hydrogen yield at thermoneutral temperatures.

to give higher hydrogen yield is highly desired. Fig. 2 shows the variation of hydrogen yield in DATR of ethanol at thermoneutral points at various pressures, CER and OER. The hydrogen yield decreases with increase in pressure at constant CER and OER, and also decreases with increase in CER at constant OER and pressure. But the hydrogen yield increases with increase in OER at constant CER and pressure. Similarly, with simultaneous increase in CER and OER, the hydrogen yield increases at constant pressure. But it decreases when CER is increased and OER is decreased at constant pressure. Simultaneous increase in pressure, CER and OER shows a mixed trend (the hydrogen yield increases at some points and decreases at other points). The hydrogen yield obtained for increase in pressure from 1 bar to 9 bar, was from 0.48 to 1.72 moles (P = 1 bar), from 0.36 to 1.51 moles (P = 3 bar), from 0.29 to 1.37 moles (P = 6 bar) and from 0.26 to 1.29 moles (P = 9 bar) at different CERs and OERs. The hydrogen yield obtained for increase in CER from 1 to 3, was from 0.56 to 1.72 moles (CER = 1), from 0.38 to 1.45 moles (CER = 2) and from 0.26 to 1.24 moles (CER = 3) for the considered pressure and OER range. The hydrogen yield obtained for increase in OER from 0.1 to 0.5, was from 0.26 to 0.87 moles (OER = 0.1), from 0.58 to 1.38 moles (OER = 0.3) and from 0.84 to 1.72 moles (OER = 0.5) for the considered pressure and CER range. The minimum hydrogen yield for every pressure was obtained at CER = 3 and OER = 0.1 and the maximum hydrogen yield was obtained at CER = 1 and OER = 0.5. Considering all the data points, the maximum hydrogen yield of 1.72 moles was observed at 1 bar pressure, CER = 1 and OER = 0.5, while the minimum hydrogen yield of 0.26 moles was observed at 9 bar pressure, CER = 3 and OER = 0.1.

3.3. CO yield at TNP

Carbon monoxide is an undesired gas for PEM fuel cell applications but a desired component of syngas for GTL (gas-to-liquids) manufacture. Fig. 3 shows the variation of CO yield in DATR of ethanol at thermoneutral points with variation in pressure, CER and OER. The CO yield decreases with increase in pressure at constant CER and OER, (but it was constant at CER = 1, OER = 0.1) and also decreases with increase in CER at constant pressure and constant OER, but the CO yield increases with increase in OER at constant pressure and constant CER. The CO yield increases at constant pressure when CER and OER are increased simultaneously. The CO yield decreases when CER is increased and OER is decreased at constant pressure. The CO yield increases when pressure is increased and CER is decreased simultaneously at constant OER. Simultaneous increase in pressure, CER and OER increases the CO yield. The CO yield obtained for increase in pressure for 1 bar to 9 bar, was from 0.07 to 0.86 moles (P = 1 bar), from 0.06 to 0.84 moles (P = 3 bar), from 0.06 to 0.82 moles (P = 6 bar), and from 0.05 to 0.8 moles (P = 9 bar). The CO yield obtained for increase in CER from 1 to 3, was from 0.12 to 0.86 moles (CER = 1), from 0.08 to 0.81 moles (CER = 2) and from 0.05 to 0.74 moles (CER = 3) for the considered pressure and OER range. The CO yield obtained for increase in OER from 0.1 to 0.5, was from 0.05 to 0.12 moles (OER = 0.1), from 0.29 to 0.43 moles (OER = 0.3) and from 0.65 to 0.86 moles (OER = 0.5) for the considered pressure and CER range. The minimum CO yield for every pressure was obtained at CER = 3 and OER = 0.1 and the maximum CO yield were obtained at CER = 1 and OER = 0.5. Considering all the data points, it was observed that a minimum of 0.05 moles of CO were produced at 9 bar pressure, CER = 3 and OER = 0.1, while a maximum of 0.86 moles were produced at 1 bar pressure, CER = 1 and OER = 0.5.

3.4. Syngas (H_2 + CO) amount at TNP

Syngas (H_2 + CO) is important for petrochemical manufacture. The conditions for maximizing syngas yield are desired. The variation in the amount of syngas moles obtained in DATR of ethanol at thermoneutral points with variation in pressure, CER and OER is shown in Fig. 4. As seen from the figure, the moles of syngas decrease with increase in pressure at constant CER and OER, and also decrease with increase in CER at constant pressure and constant OER. But the syngas yield increases with increase in OER at constant pressure and constant CER. The moles of syngas produced increase when CER and OER are increased simultaneously at constant pressure. On the other hand, the moles of syngas produced decrease when CER is increased and OER is decreased at constant

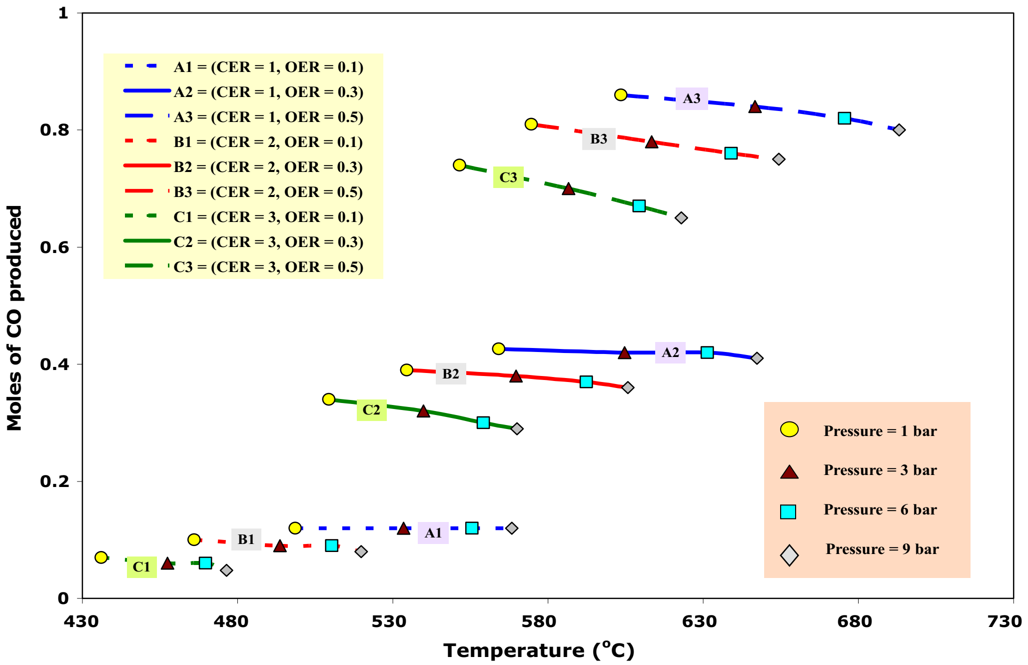

Fig. 3. Carbon monoxide yield at thermoneutral temperatures.

pressure. Simultaneous increase in pressure, CER and OER generally increases the syngas moles except for some points. The amount of syngas moles obtained for increase in pressure from 1 bar to 9 bar, was from 0.55 to 2.58 moles (P = 1 bar), from 0.42 to 2.35 moles (P = 3 bar), from 0.35 to 2.19 moles (P = 6 bar) and from 0.31 to 2.10 moles (P = 9 bar). The amount of syngas moles obtained for increase in CER from 1 to 3, was from 0.68 to 2.38 moles (CER = 1), from 0.47 to 2.26 moles (CER = 2) and from 0.31 to 1.98 moles (CER = 3) for the considered pressure and OER range. The amount of syngas obtained for increase in OER from 0.1 to 0.5, was from 0.31 to 0.98 moles (OER = 0.1), from 0.86 to 1.81 moles (OER = 0.3) and from 1.49 to 2.58 moles (OER = 0.5) for the considered pressure and CER range. The minimum syngas moles for all pressures were obtained at CER = 3 and OER = 0.1 and the maximum syngas moles were obtained at CER = 1 and OER = 0.5. Considering all the data points, the minimum amount of syngas obtained was 0.31 moles at 9 bar pressure, CER = 3 and OER = 0.1, while a maximum 2.58 moles of total hydrogen were obtained at 1 bar pressure, CER = 1 and OER = 0.5.

3.5. Syngas ratio (H_2/CO) at TNP

Lower syngas ratio (H_2/CO) between 0 and 5 is desired for converting syngas to chemicals by FT synthesis. Fig. 5 shows the variation of syngas ratio in DATR of ethanol at thermoneutral

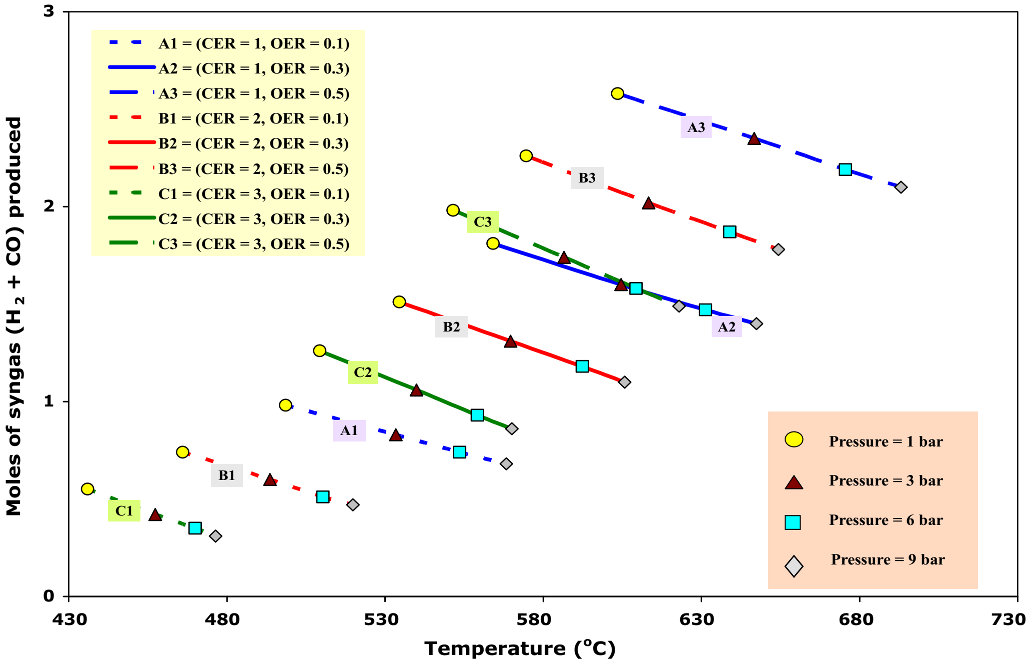

Fig. 4. Syngas yield at thermoneutral temperatures.

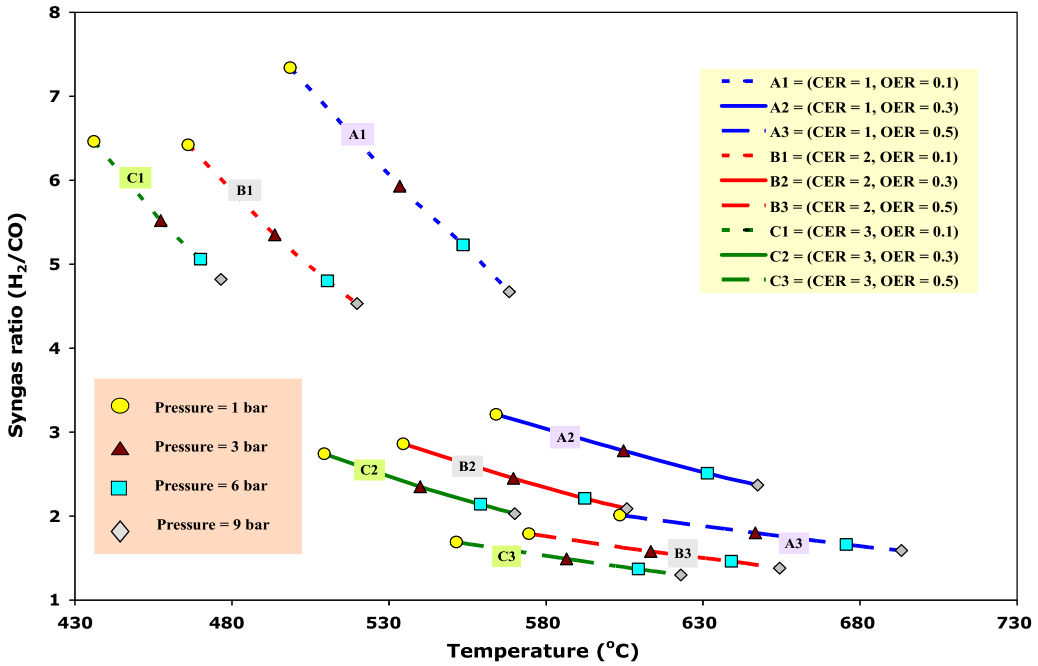

Fig. 5. Syngas ratio at thermoneutral temperatures.

points with variation in pressure, CER and OER. It was seen that the syngas ratio decreased with increase in pressure at constant CER and OER, the decrease was much more for lower OERs. With increase in OER at constant pressure and constant CER, the syngas ratio decreased considerably. Also with increase in CER at constant pressure and constant OER, the syngas ratio decreased (except at OER = 0.1). It was observed that when CER and OER were increased simultaneously, the syngas ratio decreased at constant pressure. But at constant pressure, when CER was increased and OER was decreased, the syngas ratio increased. Simultaneous increase in pressure, CER and OER decreased the syngas ratio. The range of syngas ratio obtained for increase in pressure from 1 to 9 bar, was from 1.69 to 7.34 (P = 1 bar), from 1.49 to 5.93 (P = 3 bar), from 1.37 to 5.23 (P = 6 bar) and from 1.30 to 4.82 (P = 9 bar). The range of syngas ratio obtained for increase in CER from 1 to 3, was from 1.59 to 7.34 (CER = 1), from 1.38 to 6.42 (CER = 2) and from 1.3 to 6.46 moles (CER = 3) for the considered pressure and OER range. The range of syngas ratio obtained for increase in OER from 0.1 to 0.5, was from 4.53 to 7.34 (OER = 0.1), from 2.03 to 3.21 (OER = 0.3) and from 1.30 to 2.01 (OER = 0.5) for the considered pressure and CER range. It was observed that the range of syngas ratio decreases at higher pressures. The minimum syngas ratio was obtained at CER = 3 and OER = 0.5 and the maximum syngas ratio was obtained at CER = 1 and OER = 0.1 (except at 9 bar) for all pressures considered. Considering all the data points, the minimum syngas ratio obtained was 1.30 at 9 bar pressure, CER = 3 and OER = 0.5, and maximum syngas ratio of 7.34 was observed at 1 bar pressure, CER = 1 and OER = 0.1.

3.6. *Methane formation at TNP*

Methane formation is inevitable in reforming processes. Fig. 6 depicts the variation of CH_4 formation in DATR of ethanol at thermoneutral points with change in pressure, CER and OER. It was seen that, the CH_4 formation increases with increase in pressure at constant CER and OER. It was observed that with increase in OER at constant pressure and constant CER, the CH_4 formation decreased. Also at constant pressure and constant OER, the CH_4 formation decreased with increase in CER. Similarly at constant pressure when CER and OER were increased, the CH_4 formation decreased gradually. When CER was increased and OER was decreased, the methane formation increased at constant pressure except for P = 9 bar. Simultaneous increase in pressure, CER and OER generally decreases the CH_4 formation except for some points. The moles of CH_4 obtained for increase in pressure from 1 to 9 bar was from 0.17 to 0.42 (P = 1 bar), from 0.22 to 0.49 (P = 3 bar), from 0.25 to 0.52 (P = 6 bar) and from 0.27 to 0.55 (P = 9 bar). The moles of methane obtained for increase in CER from 1 to 3, was from 0.20 to 0.55 (CER = 1), from 0.19 to 0.43 (CER = 2) and from 0.17 to 0.35 (CER = 3) for the considered pressure and OER range. The moles of methane formed for increase in OER from 0.1 to 0.5, was from 0.28 to 0.55 (OER = 0.1), from 0.22 to 0.42 (OER = 0.3) and from 0.17 to 0.33 (OER = 0.5) for the considered pressure and CER range. The minimum CH_4 yield for all pressure conditions was obtained at CER = 3 and OER= 0.5, while the maximum CH_4 was obtained at CER = 1 and OER = 0.1. Considering all the data points, minimum of 0.17 moles of CH_4 were obtained at 1 bar pressure, CER = 3 and OER = 0.5 and a maximum of 0.55 moles of CH_4 were obtained at 9 bar pressure, CER = 1 and OER = 0.1.

3.7. *Water formation at TNP*

Water formation is undesirable in reforming processes as it decreases the hydrogen yield. But water formation cannot be avoided. Fig. 7 depicts the variation in H_2O yield in DATR of ethanol at thermoneutral points at specified pressures, CER and OER. From Fig. 7, it was seen that the moles of H_2O produced increased with increase in pressure at constant CER and OER but the moles of H_2O produced decreased with increase in OER at constant pressure and constant CER. When CER was increased at constant pressure and constant OER, the moles of H_2O produced increased. Similarly, at constant pressure when CER and OER were increased simultaneously, the moles of H_2O produced increased at some points and decreased at other points. It was observed that at constant pressure when CER was increased and OER was decreased, the moles of H_2O produced gradually increased. Simultaneous increase in pressure, CER and OER generally increases the H_2O except for some points. The moles of H_2O produced for increase in pressure from 1 to 9 bar

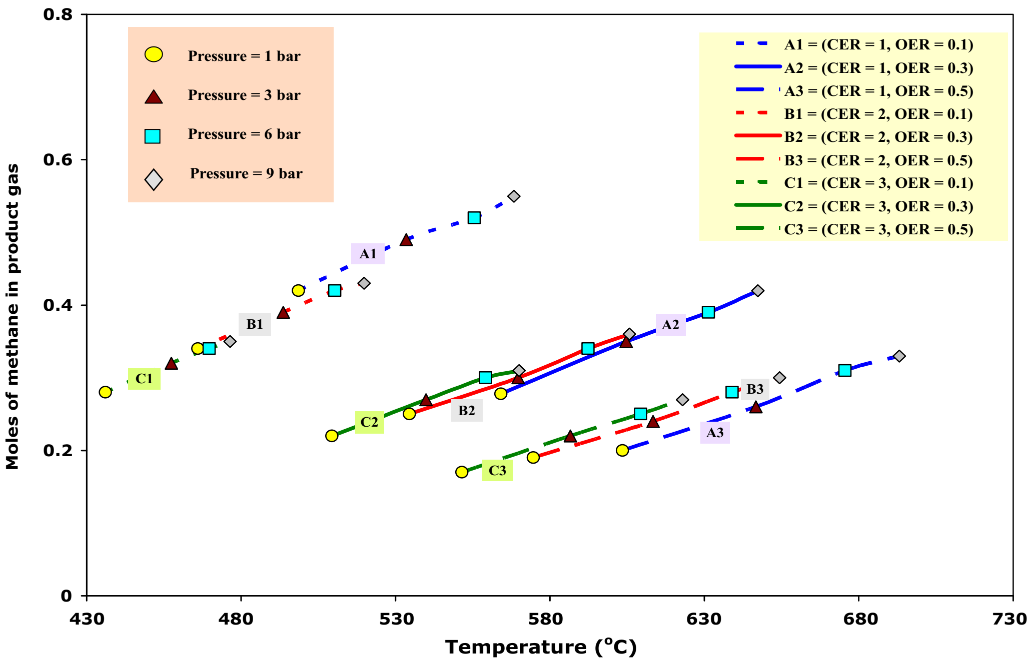

Fig. 6. Methane yield at thermoneutral temperatures.

ranged from 0.89 to 1.96 (P = 1 bar), from 0.97 to 2.0 (P = 3 bar), from 1.02 to 2.03 (P = 6 bar) and from 1.04 to 2.04 (P = 9 bar). The moles of water obtained for increase in CER from 1 to 3, was from 0.89 to 1.34 (CER = 1), from 1.18 to 1.75 (CER = 2) and from 1.41 to 2.04 (CER = 3) for the considered pressure and OER range. The moles of water formed for increase in OER from 0.1 to 0.5, was from 1.29 to 2.04 (OER = 0.1), from 1.06 to 1.80 (OER = 0.3) and from 0.89 to 1.62 (OER = 0.5) for the considered pressure and CER range. The minimum moles of H_2O for every pressure were obtained at CER = 1 and OER= 0.5 and the maximum H_2O was obtained at CER = 3 and OER = 0.1. Considering all the data points, the minimum moles of H_2O produced were 0.89 at 1 bar pressure and CER = 1 and OER = 0.5, and a maximum of 2.04 moles of H_2O were obtained at 9 bar pressure and CER = 3 and OER = 0.1.

3.8. *Carbon formation at TNP*

Carbon formation is not desirable in any process as coking may deactivate the catalyst. However, carbon (in the form of CNFs) is a valuable product for some applications. Fig. 8 shows the variation of the carbon formation in DATR of ethanol at thermoneutral points at different pressures, CER and OER. From Fig. 8, it was observed that, the carbon formation decreases with increase in pressure at constant CER and OER (except for some points). Also, it was observed that at constant pressure and constant CER, the moles of carbon formed decreased with increase in OER. However, as CER was increased at constant pressure and constant OER, the moles of carbon produced increased. It was also observed that at constant pressure when CER and OER were increased simultaneously, the

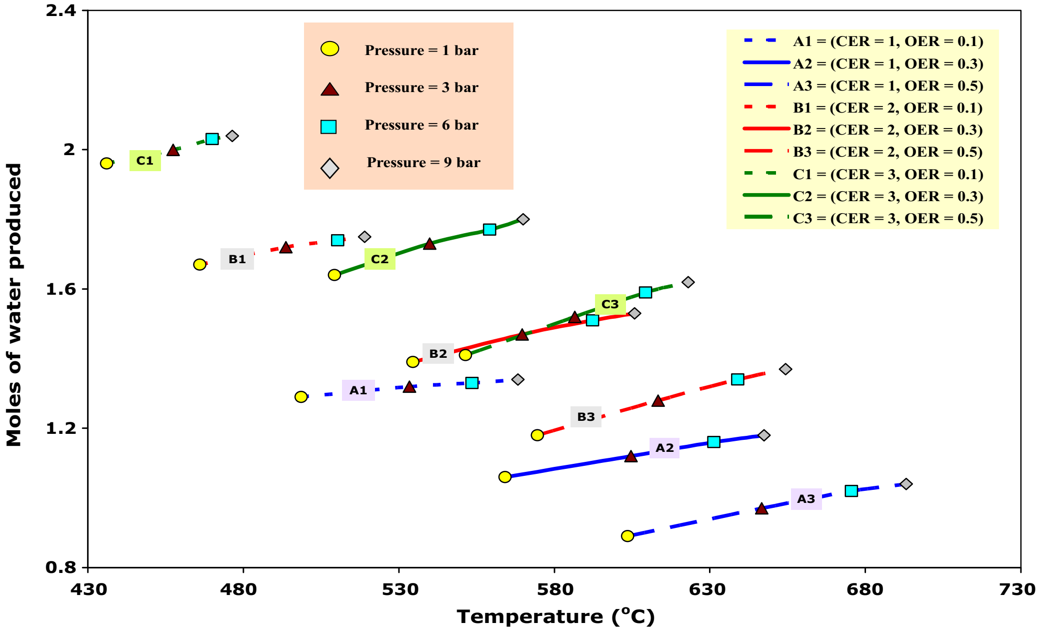

Fig. 7. Water yield at thermoneutral temperatures.

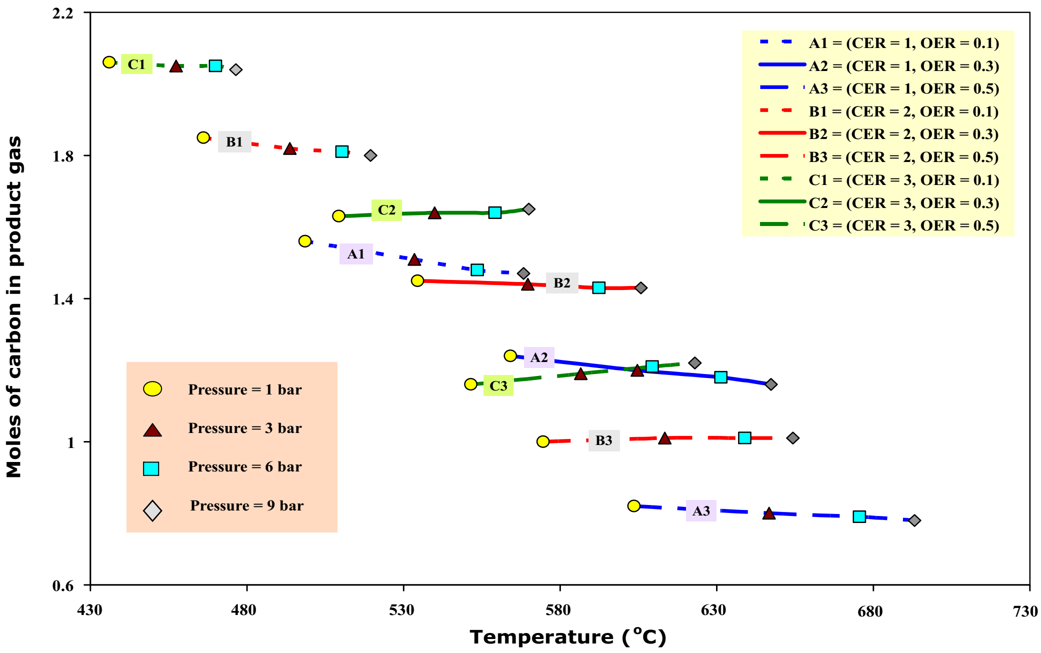

Fig. 8. Carbon yield at thermoneutral temperatures.

moles of carbon formed decreased. When CER was increased and OER was decreased, the moles of carbon formed at constant pressure increased. Simultaneous increase in pressure, CER and OER generally decreased the carbon formation except at some points. The moles of carbon formed for increase in pressure from 1 to 9 bar ranged from 0.82 to 2.06 (P = 1 bar), from 0.80 to 2.05 (P = 3 bar), from 0.79 to 2.05 (P = 6 bar) and from 0.78 to 2.04 (P = 9 bar). The moles of carbon obtained for increase in CER from 1 to 3, was from 0.78 to 1.56 (CER = 1), from 1.00 to 1.85 (CER = 2) and from 1.16 to 2.06 (CER = 3) for the considered pressure and OER range. The moles of carbon formed for increase in OER from 0.1 to 0.5, was from 1.47 to 2.06 (OER = 0.1), from 1.16 to 1.65 (OER = 0.3) and from 0.78 to 1.22 (OER = 0.5) for the considered pressure and CER range. The minimum carbon formation for all pressures was observed at CER = 1 and OER = 0.5, while the maximum carbon formation was observed at CER = 3 and OER = 0.1. Considering all the data points, the minimum carbon formation was 0.78 moles at 9 bar pressure, CER = 1 and OER = 0.5, while a maximum carbon of 2.06 moles were obtained at 1 bar pressure, CER = 3 and OER = 0.1.

3.9. CO_2 conversion (%) at TNP

CO_2 conversion in DATR of ethanol is important for CO_2 sequestration. Fig. 9 represents the variation of CO_2 conversion (%) in DATR

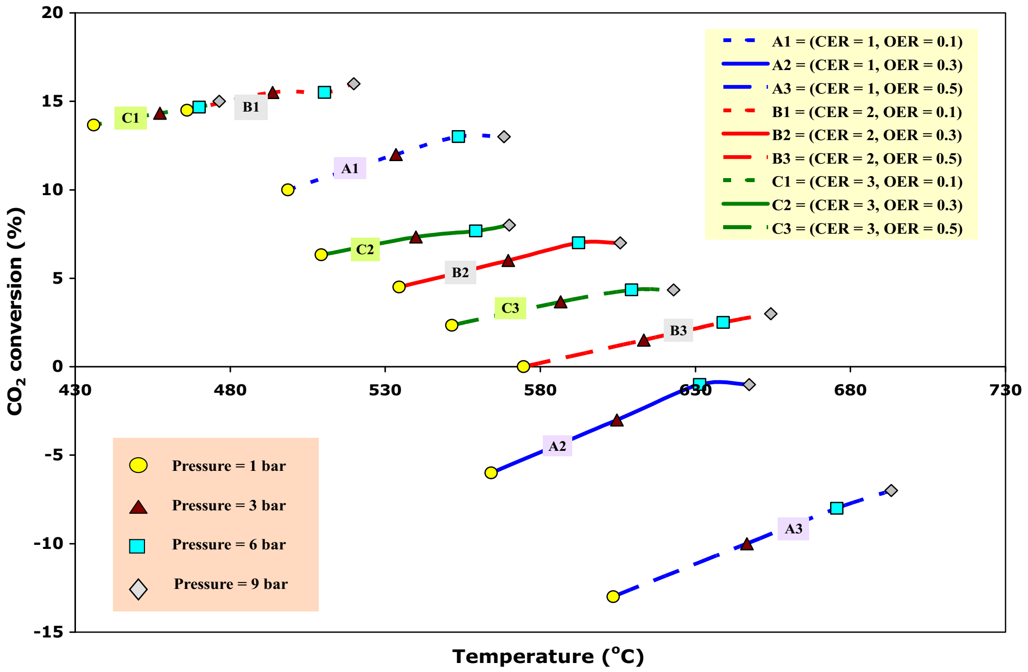

Fig. 9. Carbon dioxide conversion at thermoneutral temperatures.

of ethanol at thermoneutral point at different pressures, CER and OER. From Fig. 9, it is seen that, the CO_2 conversion increases with increase in pressure at constant CER and OER and with increase in OER at constant pressure and constant CER, the CO_2 conversion decreases. Also at constant pressure and constant OER, the CO_2 conversion increases (except for OER = 0.1) with increase in CER of the process. Also at constant pressure when CER is increased and OER is decreased, the CO_2 conversion increases. Simultaneous increase in pressure, CER and OER generally decreases the CO_2 conversion except for some points. The CO_2 conversion (%) obtained for increase in pressure from 1 to 9 bar ranged from −13.0 to 14.5 (P = 1 bar), from −10.0 to 15.5 (P = 3 bar), from −8.0 to 15.5 (P = 6 bar) and from −7.0 to 16.0 (P = 9 bar). The CO_2 conversion (%) obtained for increase in CER from 1 to 3, was from −13.00 to +13.00 (CER = 1), from 0.00 to 16.00 (CER = 2) and from 2.33 to 15.00 (CER = 3) for the considered pressure and OER range. The CO_2 conversion (%) obtained for increase in OER from 0.1 to 0.5, was from 10.00 to 16.00 (OER = 0.1), from −6.00 to 8.00 (OER = 0.3) and from −13.00 to 4.33 (OER = 0.5) for the considered pressure and CER range. The minimum CO_2 conversions were obtained at CER = 1 and OER = 0.5 and the maximum CO_2 conversions were obtained at CER = 2 and OER = 0.1 for all the pressures. The CO_2 conversion varied from a minimum of −13% at 1 bar pressure, CER = 1 and OER = 0.5 to a maximum of 16% at 9 bar pressure, CER = 2 and OER = 0.1, for all the data points considered.

4. Conclusions

The product composition at thermoneutral points for DATR of ethanol at various pressures showed some interesting results. Maximum carbon formation was observed at OER = 0.1 and CER = 3 and it decreased with increase in pressure; hence thermo-neutral low pressure operation can be used to produce carbon (possibly CNFs). The syngas ratio ranged between 7.34 to 1.30 and the syngas ratio decreased with increase in pressure, and as lower syngas ratios are desirable for petrochemical manufacture by FT synthesis, thermoneutral higher pressure operation can be used for this purpose. The maximum syngas (total H_2) was formed at CER = 1 and OER = 0.5, and it reduced with increase in pressure, so lower pressure TNP operation can be used for hydrogen/syngas manufacture for fuel cells. Higher CO_2 conversion was observed for CER = 2 and OER = 0.1 and higher pressures making this process effective for CO_2 conversion (CO_2 sequestration). Thermoneutral points ranged from 436.05 to 693.15 °C which are practically achievable temperatures in ethanol chemical processes. Depending upon the desired product requirements, the system pressure and thermoneutral points can be chosen for process operation. Syngas (of a particular ratio), carbon (in the form of CNFs), syngas moles (total H_2) are the usual desired products. A maximum of 2.58 moles of total hydrogen obtained at 1 bar, CER = 1 and OER = 0.5 producing 0.82 moles of carbon, of syngas ratio 2.01 with 0.20 moles of CH_4 and 0.89 moles of water for the TNP = 603.55 °C was found to be the best operating thermoneutral point for value added product generation. Lower pressure TNP operation is favored for higher hydrogen production, lower methane and water formation. Higher pressure TNP operation is favored for lower syngas ratio with higher CO_2 conversion and sometimes lower carbon formation.

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