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Study of Process Factor Effects and Interactions in Synthesis Gas Production via a Simulated Model for Glycerol Steam Reforming

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Abstract:

With the continual global focus in biodiesel production, a glut of glycerol (it's by-product) is expected in the world market. One viable and proven possibility in utilising the less useful and desired glycerol as a source for the production of hydrogen via the steam reforming and water gas shift process. This study is essentially and in-depth investigation of the interaction of the key process factors and their effect on the selectivity of Hydrogen from the process. The basis of the investigation was a simulated model of the steam reforming process using ASPEN plus V8.8. Results were obtained according to the optimisation plan developed using central composite design (CCD). The variables (and range) were temperature (700°C – 1100°C), Pressure (0.1 atm – 1.9 atm) and steam to glycerol ratio (1 mol/mol – 12 mol/mol). The results of optimisation showed that maximum yield of H_2 and minimal methanation can be obtained at a temperature of 900°C , an STGR of 15.75 mol/mol and at atmospheric pressure. The optimum result was predicted by the simulation as $\text{H}_2 = 66.72\%$, $\text{CO} = 11.76\%$, $\text{CO}_2 = 21.52\%$ and $\text{CH}_4 = 0\%$. Sensitivity analysis was carried out to show that Hydrogen production is favoured at higher temperatures and methanation at lower temperatures respectively. A critical investigation of the factor effects and interactions for each product in the synthesis gas (dry basis) was also carried out using response surface methodology.

Keywords: synthesis gas, steam reforming, glycerol, water gas shift, central composite design, aspen plus v8.8

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1 Introduction

Considerable effort and resources are currently being channelled into the development of alternative energy from biological and natural sources. Chief among them is the production of biodiesel from the transesterification of oils. Biodiesel is bio-degradable, non-toxic and environmentally friendly [1]. The by-product of the process is glycerol ($\text{C}_3\text{H}_8\text{O}_3$). In converting vegetable oils into biodiesel, approximately 10% (w/w) of glycerol is produced as a by-product [2].

With the continual increase in biodiesel production, a glut of glycerol is expected in the world market. Currently, there are many applications of glycerol and these include personal care products, food, oral care, tobacco, and polyurethane production [3]. Most by-product glycerol is sent to water treatment for digestion but this process is slow, expensive and demonstrates low yield. It also can be purified by distillation. However, this is an expensive process and the low market cost of glycerol makes it uneconomic [4]. The glycerol price dropped by two-thirds within the last decade [3] because of surplus amounts in the market and is still dropping in the current decade. There is a current search for more alternative uses of glycerol as Increasing production of biodiesel will lead to glycerol supply exceeding demand.

One viable and proven possibility is using it as a source for the production of hydrogen. Gasification and aqueous phase reforming are also other processes of producing hydrogen from bio-based sources [5]. Bio-resources based processes for Hydrogen gas synthesis are seen as viable options for the future due to their theoretically carbon-neutral nature. Hydrogen poses no environmental problem and also does not contribute to atmospheric carbon dioxide emissions [6]. Alongside glycerol, pyrolysis oil (another bio-resource) also interestingly has been proved to be okay for steam reforming for hydrogen production [7, 8]. At present, almost 95% of the hydrogen produced is obtained from fossil fuel based feedstock [9] and it is used majorly as a chemical ingredient in petrochemical, metallurgical, food, and electronics processing industries. Also, the global demand

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for hydrogen gas, is growing due to the technological advancements in fuel cell industry [9]. Hydrogen gas possesses the highest energy content per unit of weight (120.7 kJ/g), compared to any of the known fuels [10].

The steam reforming of Glycerol has been extensively studied experimentally over the years with much focus on energy and exergy analysis [11], kinetic modelling and thermodynamic analysis [3, 12–19], sorption enhancement techniques [14, 20], the minimisation of carbon deposition and the trials and effectiveness of different catalyst [2, 5, 9, 12, 21–29].

Several simulation studies has also been carried out on the steam reforming of glycerol [30, 31] but the focus was majorly on gas flow patterns and velocity. Several factors affect the reactions involved in the steam reforming of glycerol. Among them are reaction temperature, system pressure and steam to glycerol ratio [12]. This study is essentially and in-depth investigation of the interaction of these key factors and their effect on the selectivity of Hydrogen from the process. The basis of the investigation will be a simulated model of the steam reforming process using ASPEN plus V8.8. The model will serve as a reference system [32] to identify reaction responses to the different factors and how they interact.

2 Methodology

Steam reforming is a high temperature process whereby Glycerol is converted to a Hydrogen rich gaseous product known as synthesis gas. The chemical reactions involved in the steam reforming of glycerol into synthesis gas are well understood and have been properly studied [24, 27, 33]. eqs (1–3) give a sequence of the reaction.

1. Glycerol decomposition;



2. Water-Gas Shift reaction;



3. Methanation reaction;



The combination of reactions (1) and (2) gives the overall equation of reaction as considered in this study.

2.1 Performance parameters

The key performance parameters of the system are the reaction conversion, the yield of hydrogen, and the extent of carbon deposition. Studying the system of eqs (1–3), it will be noticed that reaction conversion will essentially always be 100 %. This is due to the fact that glycerol decomposition is in the presence of steam, but this cannot be adequately expressed directly while specifying the equations in ASPEN Plus. In practice, there is a wide range of parameter allowance for which the reaction will always proceed to 100 % completion. Coupled with the fact that metal catalysts are generally used in the industry for the process conversion is not our interest as maximum conversion can be easily achieved. The eqs (4–7) were used to calculate the performance of the system.

$$H_2\% \text{Molar composition} = \frac{\text{moles of } H_2}{\text{Total moles of syn - gas (dry basis)}} \times 100\% \quad (4)$$

$$CO\% \text{Molar composition} = \frac{\text{moles of } CO}{\text{Total moles of syn - gas (dry basis)}} \times 100\% \quad (5)$$

$$CO_2\% \text{Molar composition} = \frac{\text{moles of } CO_2}{\text{Total moles of syn - gas (dry basis)}} \times 100\% \quad (6)$$

$$CH_4\% \text{Molar composition} = \frac{\text{moles of } CH_4}{\text{Total moles of syn - gas (dry basis)}} \times 100\% \quad (7)$$

The Optimisation goal is to maximise the hydrogen gas yield from the system, and to minimise methanation. The key factors affecting the performance parameters/system responses are Reaction Temperature, Pressure and steam to glycerol ratio (STGR).

2.2 Simulation methodology

In ASPEN Plus V8.8 the components are classified into several major classes. In this work, only conventional components are involved. In the global settings of the simulation, the stream class is set to CONVEN. The components added to the simulation were Glycerol, carbon monoxide, carbon dioxide, methane, hydrogen, and water. The property method selected for the simulation was UNIFAC. The UNIQUAC Functional Group Activity Coefficient model (UNIFAC) is an improvement on the UNIQUAC model as it incorporates the functional group of the chemical species as one of the basis for determining activity coefficients. UNIFAC is quite accurate for low pressure systems (1–5 bars). Also, UNIFAC in ASPEN plus uses Redlich-Kwong equation of state which is also accurate for calculations on chemical systems such as those involving synthesis gas. The reformer was modelled in the simulation by an equilibrium reactor (REQUIL). The equations of reaction stated earlier were specified in the reactor block. Reduction of product vapour temperature to induce condensation of water vapour is modelled by a heater set to ambient conditions.

2.3 Simulation environment

The design of the simulation was done specifically with the aim of studying the interaction of factors for the glycerol steam reforming process. Hence, a simple approach/design will be utilised focusing mainly on the REQUIL block. The flow diagram of the process is given in Figure 1.

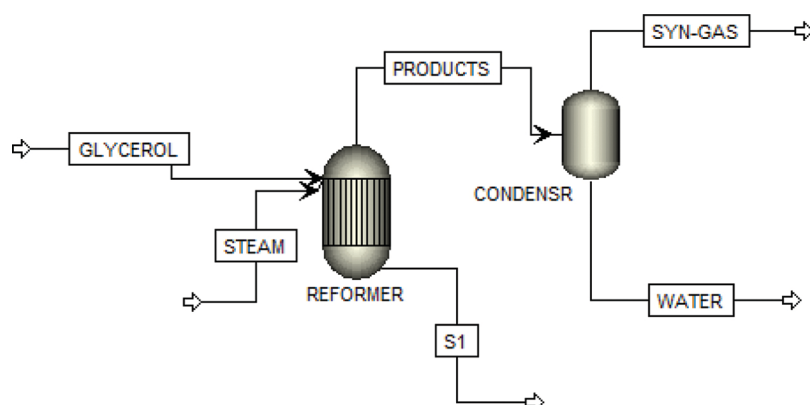


Figure 1: Process flow diagram of the simulation.

Glycerol at ambient conditions and steam at 150⁰C was sent into the reformer at a specific molar ratio. The steam reforming reactions take place at set temperature and pressure of the equilibrium reactor. The Steam to glycerol ratio (STGR), reactor temperature, and reactor pressure can be easily varied from the simulation. The stream S1 does not have any flowrate as the reaction occurs entirely in the vapour phase. However, it is placed there as ASPEN Plus always require the specification of a liquid stream for an equilibrium reactor. The products vapour is condensed back to ambient conditions to remove any excess water from the gas stream and then to consequently obtain synthesis gas.

2.4 Optimisation studies

Central Composite Design (CCD) was used to design the experiments for the study of factor interactions and effects and the determination of optimum parameters for the steam reforming of glycerol. Design-Expert 10.0 was utilised for this purpose. In order for more convenient report, notations in Table 1 were given to the factors/independent variables.

Table 1: Notations of factors/independent variables.

Notation	Factor	Unit
A	Reaction Temperature	⁰ C
B	Reactor Pressure	atm
C	Steam-to-Glycerol Ratio (STGR)	Mol/mol
Y1	H ₂ % Molar Composition	%

Y2	CO % Molar Composition	%
Y3	CO ₂ % Molar Composition	%
Y4	CH ₄ % Molar Composition	%

The lower and upper limits of the independent variables in the experimental plan were fixed as presented in Table 2.

Table 2: Upper and lower limits of variables.

S/N	Factor	Lower Limit	Upper Limit
1	A	700	1100
2	B	0.1	1.9
3	C	1	12

3 Results and discussion

3.1 Model results and validation

The result for Hydrogen gas obtained from the system with respect to temperature and pressure variations are plotted below and validated with experimental work [3] to demonstrate the relevance and adequacy of the model.

Figure 2 shows a remarkable consistency between simulation model results and experimental results by [3]. For the results shown above, [3], utilised a steam to gas ratio of 9:1 while varying temperature from 600 K to 1000 K. The operation was done at two pressures; 1 and 5 atm. The unit on the y-axis of the plot is the number of moles of Hydrogen gas produced from the process per mole of glycerine (as presented by [3]). From the simulation, the corresponding results were easily computed from molar flowrates of the glycerine in the feed stream in relation to the Hydrogen gas in the product stream. This value is a ratio hence it is independent of the magnitudes of the feed stream. The simulation results for the exact same conditions are placed alongside. The model can be said to be valid in representing the steam reforming of glycerol to form synthesis gas. At 1 atm, simulation model result has a correlation coefficient of 1.00 with experimental work while at 5 atm, correlation is at 0.995. The simulation result is still consistent with those obtained by [16].

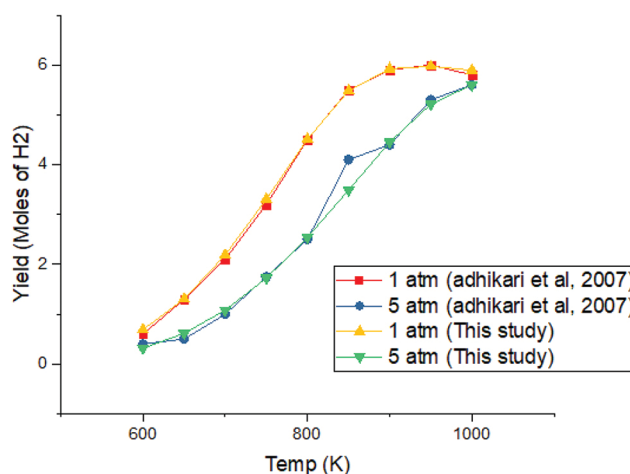


Figure 2: Model validation with [3].

The simulation results were furthermore examined by the products distribution in the synthesis gas. The results of [4], was used to validate the model. The results above by [4], were obtained at steam/carbon ratio of 1.35, a glycerol feed-rate of 0.0065 ml/min and 1 atm pressure. The results from the simulation are at similar S/C ratio, temperature and pressure conditions albeit at a feed-rate of 100 mol/hr. Considering that mole fractions are being compared the feed-rates due not bear any significance on the results. The simulation model shows considerable similarity with the experimental result. There is a fairly good correlation of the yields of all products with experiments except at temperatures below 700 °C. We can say with a good measure of confidence that the model is in good agreement with experimental results for the steam reforming of glycerol.

3.2 Optimisation

The response of the Central Composite Design (CCD) used to design the experiments for the study of factor interactions and effects and the determination of optimum parameters for the steam reforming of glycerol is given in Table 3. Design-Expert 10.0 was utilised for the analysis of factors and their interactions. Some of the values of factors 1, 2 and 3 in Table 3 are outside the range of the upper and lower limits set in Table 2. This is because Central Composite Design is a statistical tool for optimisation. Each experimental run is either a center point or an axial point in the design matrix. Typically, axial points will sometimes fall outside the factor limits. There are no negative temperatures (factor 1) in the experimental runs. The negative pressure in factor 2 (run 3) was taken as positive on the simulation as it is considered that the magnitude of the pressure only denotes effective pressure. Also, ASPEN Plus does not facilitate the input of negative pressure in the simulation. For Factor 3 (row 17), we have a negative steam-to-gas-ratio (STGR). This is obviously not physically possible as the value is simply a ratio of the two reacting feedstock, hence the positive value will be utilised and the model is validated in Figure 3.

Table 3: The response of CCD.

Run	Factor 1 A: Temperature	Factor 2 B: Pressure	Factor 3 C: STGR	Response 1 H ₂ % Molar Composition	Response 2 CO % Molar Composition	Response 3 CO ₂ % Molar Composition	Response 4 CH ₄ % Molar Composition
	Celsius	Atm	mol/mol	%	%	%	%
1	900	1	6.5	64.207	20.17	15.62	0.003
2	1100	1.9	1	58.9	38.33	2.77	0
3	900	-0.513614	6.5	64	20.29	15.71	0
4	1236.36	1	6.5	62.2	26.3	11.49	0
5	700	0.1	12	67.77	9.12	23.11	0
6	1100	1.9	12	65	18.24	16.76	0
7	700	1.9	1	50.79	28.8	11.11	9.3
8	700	1.9	12	67.03	9	23.52	0.45
9	900	1	6.5	64.207	20.17	15.62	0.003
10	700	0.1	1	59.53	33.33	6.4	0.74
11	900	1	6.5	64.207	20.17	15.62	0.003
12	1100	0.1	12	65	18.26	16.74	0
13	900	1	6.5	64.207	20.17	15.62	0.003
14	900	1	15.7499	66.29	11.78	21.55	0.38
15	1100	0.1	1	58.92	38.29	2.79	0
16	900	1	6.5	64.207	20.17	15.62	0.003
17	900	1	-2.74986	61.65	29.18	9.17	0
18	900	1	6.5	64.207	20.17	15.62	0.003
19	900	2.51361	6.5	63.84	20.28	15.71	0.17
20	563.641	1	6.5	60.73	7.17	26.29	5.81

3.3 Selectivity to pressure

Little variability was given for pressure because previous research [3, 12] has reliably informed that atmospheric pressure is the optimum pressure level for glycerol steam reforming. The simulation was run at different pressures (Figure 4) with an STGR of 10:1 to reinforce this. It can be easily deduced that optimum pressure is somewhere near atmospheric pressure. In his study, [16], presented a similar behaviour for the H₂ selectivity with pressure.

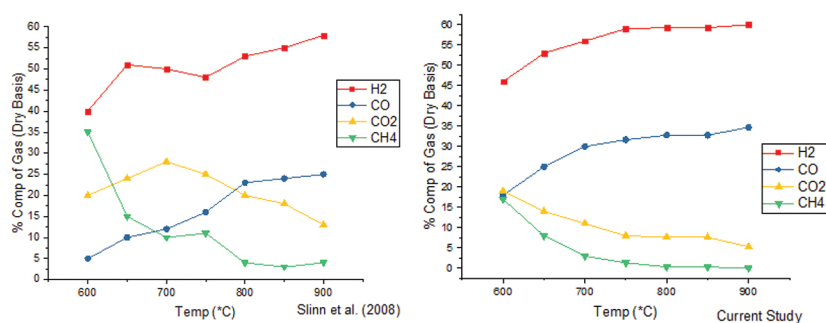


Figure 3: (a–b) Model validation with [4].

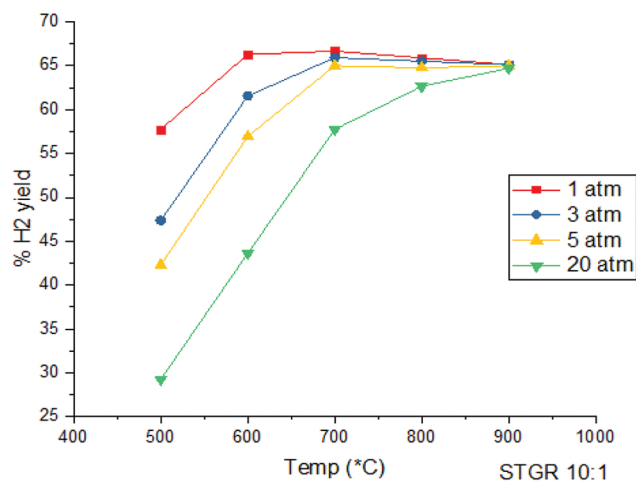


Figure 4: H₂ selectivity to pressure.

Optimisation goals were to maximise H₂ selectivity and minimise methanation. Apart from the atmospheric pressure that was set to 1 atm, the other factors were ranges as similar to the limits in the initial design of experiments. The results of optimisation showed that maximum yield of H₂ and minimal methanation can be obtained at a temperature of 900 °C, an STGR of 15.75 mol/mol and at atmospheric pressure. The desirability of the result was 1.000. Design expert also gave the results from the optimum factors as H₂ = 67.77 %, CO = 9.38 %, CO₂ = 22.8 % and CH₄ = 0 %. However, for higher accuracy the optimum parameters were taken to the ASPEN Plus simulation to the obtain optimum results as H₂ = 66.72 %, CO = 11.76 %, CO₂ = 21.52 % and CH₄ = 0 %.

3.4 Sensitivity analysis

The simulation temperature sensitivity (Figure 5) is in good agreement with experimental results [3, 4, 12, 24]. CO and CO₂ are considered impurities as they do not compete with Hydrogen gas production. However, CO is more desired in the gas stream because it is combustible. However, they are good indicators of the extent of steam reforming reaction and water-gas shift reaction respectively. Hydrogen production is favoured at higher temperatures because of the endothermic nature of the reaction. Methanation is favoured at lower temperatures. Temperature rise will therefore lead to a drop in methanation and an increase in temperature until the optimal threshold is exceeded.

3.5 Factor effects and interactions for H₂ production

The Different factors have combinatory effects on the Hydrogen gas selectivity of the process. Taking a look at the Figure 6(a–c) a lot can be understood about the process.

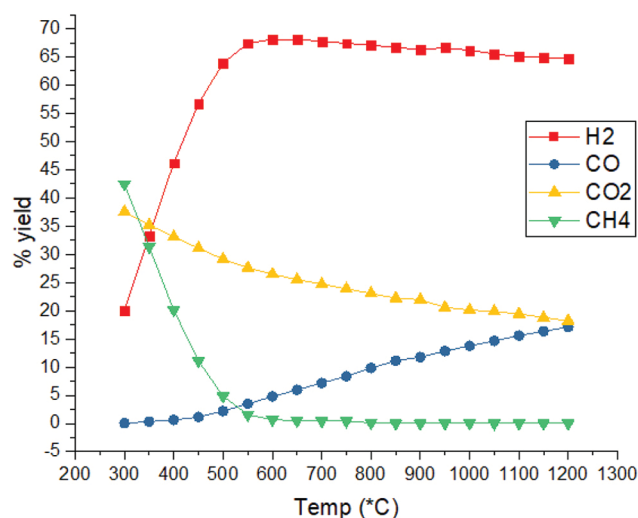


Figure 5: Temperature sensitivity of products at optimum STGR and pressure.

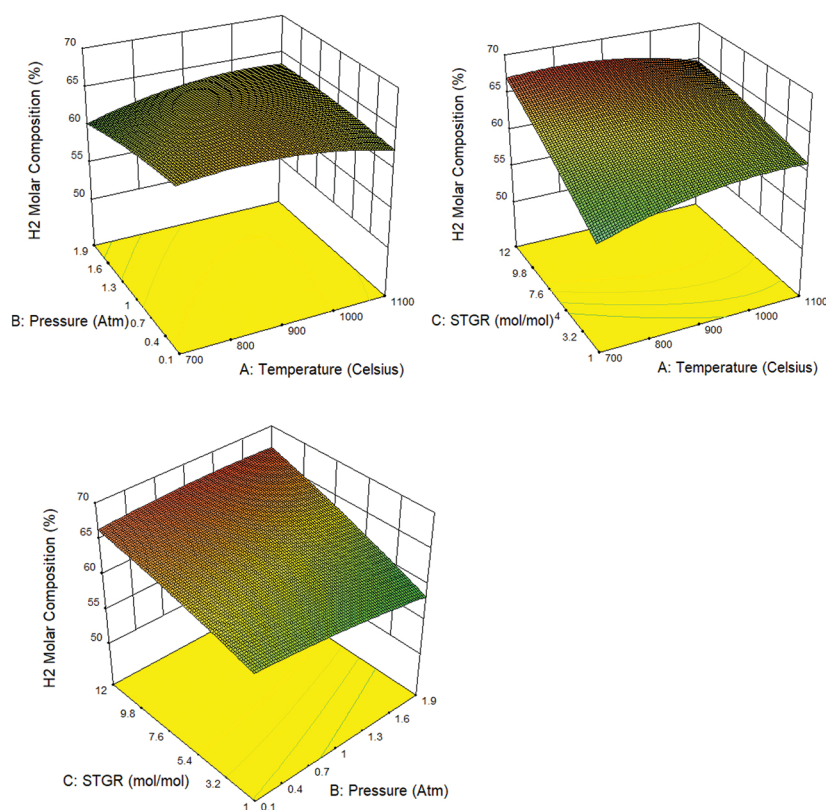


Figure 6: (a–c) Response surface plots for effects and interactions on H_2 production.

In the domain of all pressures, Hydrogen gas selectivity generally rises with temperature until the optimum temperature is exceeded before it starts to fall. Higher STGR favours Hydrogen gas production and this effect is more pronounced at lower temperature than at higher temperatures. Irrespective of pressure, STGR increase favours Hydrogen selectivity.

3.6 Factor effects and interactions for CO production

As presented in the system of equations utilised in developing the model, CO is produced in glycerol decomposition and used up in the water gas shift and methanation reactions. Hence, the CO in the system gives an indication of the extent to which the combination of factors favour glycerol decomposition over the other reactions.

Temperature increase favours CO production and this seems fairly independent of slight pressure changes. CO production falls with increasing STGR and this trend is similar at all temperatures. CO production also falls

with increasing STGR for slight pressure change. Generally, we notice a fall in CO production due to a rise in STGR. This is due to the fact that more steam in the system will favour the water gas shift reaction which is a CO consuming process.

3.7 Factor effects and interactions CO₂ production

CO₂ is produced as a by-product of the water gas shift reaction hence the CO₂ production is a very good indicator of how these factors interact to affect the reaction.

From Figure 8(a–b), we see that CO₂ production falls with increasing temperature and this is quite independent of pressure. This temperature behaviour is due to the water gas shift reaction being exothermic. Heat releasing reactions will always proceed faster at lower temperatures and vice-versa. A retardation of the water gas shift reaction (a CO consuming and CO₂ producing reaction) will favour a higher CO content (Figure 7) and lower CO₂ content in the product. There is a steep climb in CO₂ with increasing STGR and this is more pronounced at lower temperatures. Also, CO₂ production is also favoured at higher STGR for all slight pressure changes. This gives a general indication of the importance of excess steam in favouring an increase in CO₂ (and consequently hydrogen). Excess steam will always favour the water gas shift reaction. In economically optimising the process, it will be more favourable to reduce steam input (STGR) to reduce the CO₂ formation albeit keeping an eye on the Hydrogen gas production (as steam also favours Hydrogen gas production too)

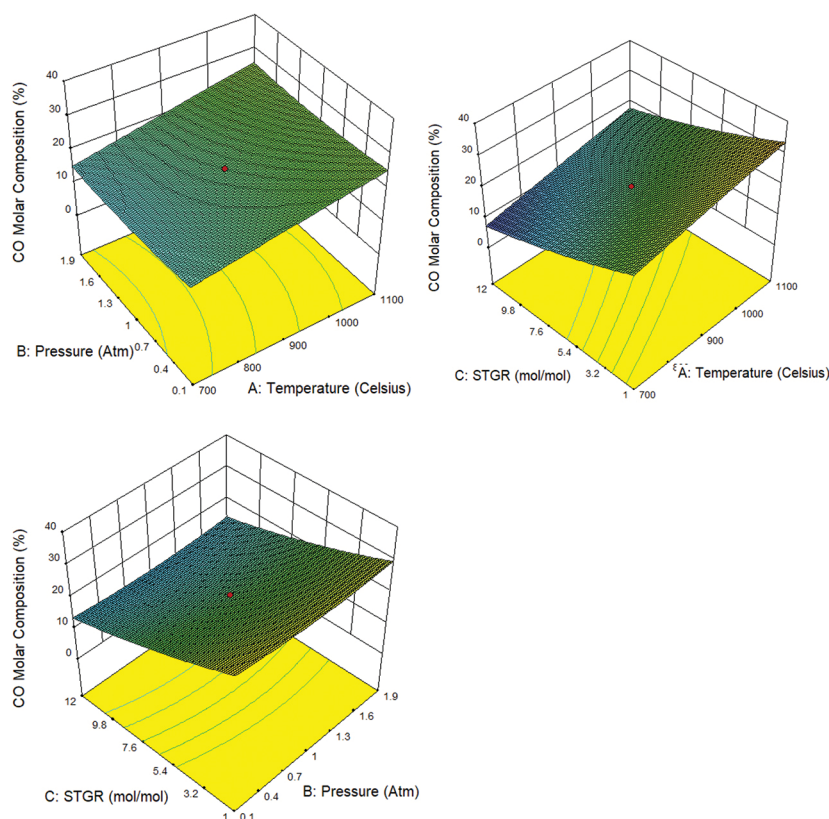


Figure 7: (a-c) Response surface plots for effects and interactions on CO production.

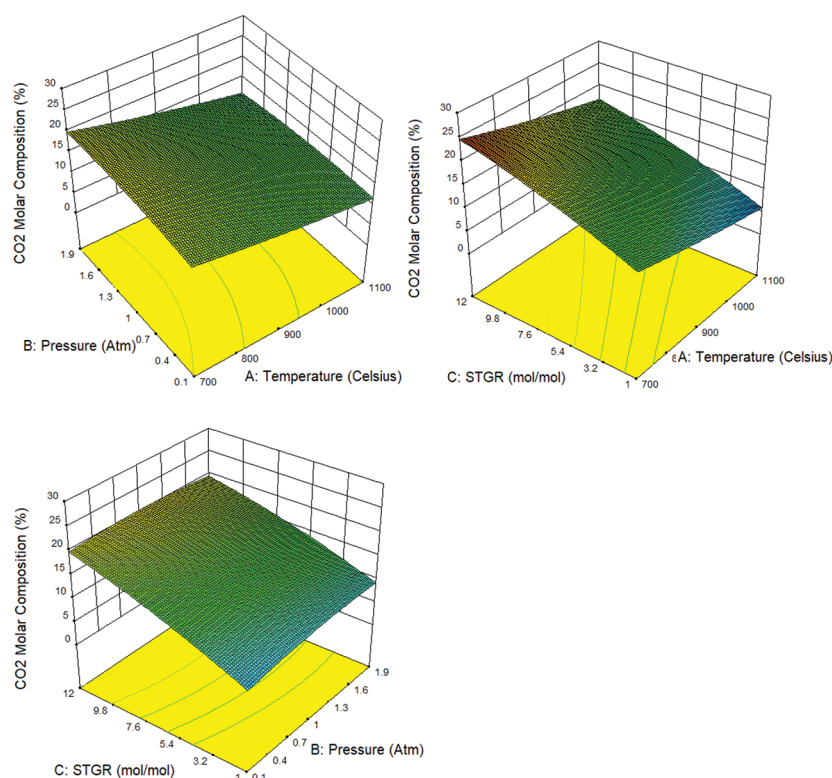


Figure 8: (a-c) Response surface plots for effects and interactions on CO₂ production.

3.8 Factor effects and interactions CH₄ production

Methane is formed from methanation reaction therefore it's production will be an easy indication of the reaction extent (Figure 9).

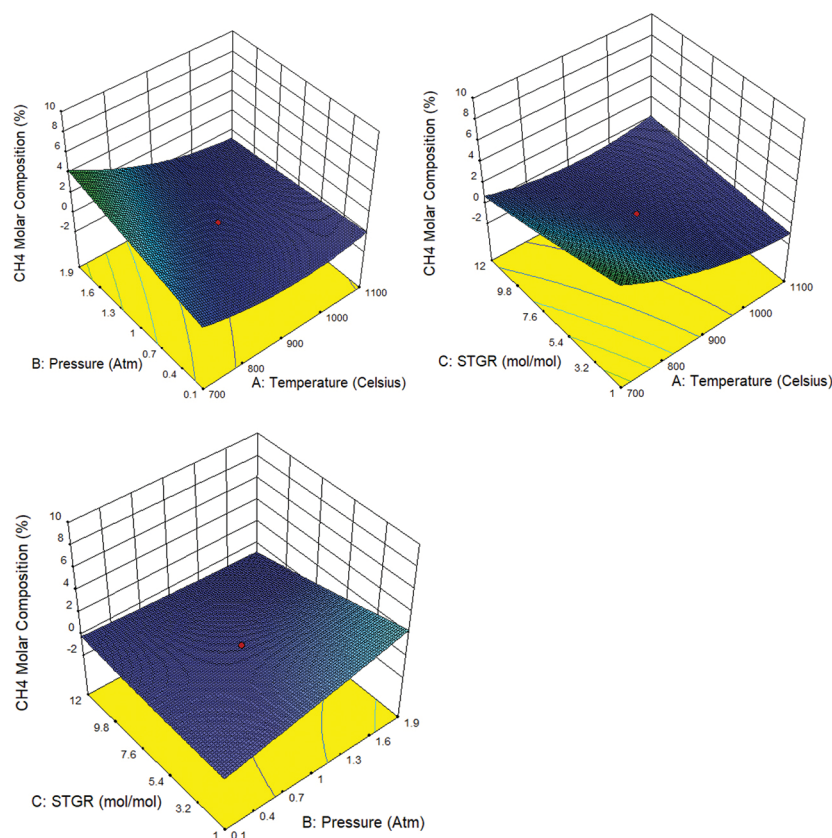


Figure 9: (a-c) Response surface plots for effects and interactions on CH₄ production.

There is a steep rise in methane yield at lower temperatures and higher pressures. Methanation reaction is an exothermic reaction hence will be favoured at lower temperatures. Methane production also climbs at lower STGR and temperature. Higher pressures will always favour methane production and this is fairly independent of STGR. Generally, lower temperatures, lower STGR and higher pressures favour methane production in the process.

4 Conclusion

The simulation model was prepared using ASPEN Plus v8.8 and was summarily validated with experimental results. Results were obtained according to the optimisation plan developed using central composite design (CCD). The variables (and range) were temperature ($700^{\circ}\text{C} - 1100^{\circ}\text{C}$), Pressure (0.1 atm – 1.9 atm) and steam to glycerol ratio (1 mol/mol – 12 mol/mol). The results of optimisation showed that maximum yield of H_2 and minimal methanation can be obtained at a temperature of 900°C , an STGR of 15.75 mol/mol and at atmospheric pressure. The desirability of the result was 1.000.

The optimum parameters were taken to the ASPEN Plus simulation to obtain optimum results as $\text{H}_2 = 66.72\%$, $\text{CO} = 11.76\%$, $\text{CO}_2 = 21.52\%$ and $\text{CH}_4 = 0\%$. Sensitivity analysis was carried out to show that Hydrogen production is favoured at higher temperatures and methanation is favoured at lower temperatures. A critical investigation of the factor effects and interactions for each product in the synthesis gas (dry basis) was also carried out.

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