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Greener synthesis of butylene carbonate via CO_2 utilisation using graphene-inorganic nanocomposite catalysts

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Abstract. The synthesis of butylene carbonate (BC) through the reaction of butylene oxide (BO) and carbon dioxide has been investigated using highly efficient graphene-inorganic heterogeneous catalyst, lathana-cerium-zirconia and graphene oxide represented as La– Ce–Zr–GO nanocomposite. The catalysts have been extensively characterised using transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area measurement powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analysis. Response Surface Methodology (RSM) using Box-Behnken Design (BBD) has been applied to optimise the single and interactive effect of four independent reaction variables, i.e. temperature, pressure, catalyst loading and time, on the conversion of BO and BC yield. Two quadratic regression models have been developed representing an empirical relationship between each reaction response and all the independent variables. The predicted models have been validated statistically and experimentally, where the high agreement was observed between predicted and experimental results with approximate relative errors of ±1.5% for both the conversion BO and the yield of BC.

Key-words. Butylene carbonate (BC), carbon dioxide (CO_2) utilisation, continuous hydrothermal flow synthesis (CHFS), Box-Behnken Design (BBD), lathana-cerium-zirconia and graphene oxide nanocomposite (La-Ce-Zr/GO).

1.0 INTRODUCTION

The utilisation of carbon dioxide (CO_2) into valuable chemicals has drawn much attention due to the growing concerns about the severe impact of greenhouse gas on global warming and also an unprecedented climate change in recent times[1,2].The continuous emission of CO_2 into the atmosphere has reached an unsustainable level and therefore there is an urgent need to reduce the emission of CO_2 [3]. CO_2 plays an important role in every living thing in the world, especially in a chemical industry as a building block due to its thermodynamic stability and chemical inertness. CO_2 is regarded as a stable compound because of its carbon which covalently bonded to two oxygen atoms, although the thermodynamic stability of CO_2 requires a significant amount of energy to be decomposed [4–6]. The reactions of CO_2 with epoxides are exothermic and generate an organic carbonate.

The conversion of CO_2 into valuable chemicals such as organic carbonates, which are acyclic, cyclic and polycyclic carbonates, and widely used chemicals in agriculture, automobile, cosmetic, lithium battery, paint and pharmaceutical industries [4,7–9].

Butylene carbonate (BC) is an excellent reactive intermediate material that is used for the production of surfactant, plasticisers, polymers and also uses as a solvent for wood binder resins, foundry sand binders, degreasing, paint remover, lubricants as well as lithium battery due to its high polarity property [4].

A rapid, greener continuous hydrothermal flow synthesis (CHFS) reactors have been considered for catalyst preparation in order to improve the catalyst stability and enhance performance. Response Surface Methodology (RSM) is a collection of mathematical techniques based on multivariate statistics, which includes experimental design, statistical modelling, and process optimisation. Recently, the use of RSM has been used to evaluate several relationships of multiple process variables with the aim to optimise a specified response [10].

In this study, BC synthesis via CO_2 utilisation using graphene inorganic nanocomposite catalysts has been investigated. Box Behnken Design (BBD) from RSM has been conducted to evaluate process optimisation, with the aim to understand the relationships between four operating variables that include catalyst loading (w/w), reaction temperature, pressure, and reaction time on conversion of BO and yield of BC. Two quadratic regression models have been developed representing an empirical relationship between each reaction response and all the independent variables. They have been used to establish the optimum operating reaction conditions for BC synthesis.

2.0 EXPERIMENTAL

2.1 Materials

Natural graphite powder, hydrochloric acid, sulphuric acid, sodium nitrate, potassium hydroxide pellet, hydrogen peroxide, acetone, octane, and potassium permanganate were purchased from Fisher Scientific UK Ltd. Methanol, cerium(III) nitrate hexahydrate, Lanthanum (III) nitrate hexahydrate, zirconium (IV) oxynitrate hydrate, butylene oxide, butylene carbonate were purchased from Sigma–Aldrich Co. LLC, UK. The catalysts used for the experiments were magnesium oxide, titanium silicate, zirconium oxide, cerium oxide, lanthana oxide, lanthana doped zirconia, lithium doped zirconia, zirconium-doped hydrotalcite, ceria doped zirconia and lanthana, ceria doped zirconia were supplied by MEL Chemicals Company except for magnesium oxide and titanium silicate which were purchased from Sigma Aldrich. The liquid CO_2 cylinder (99.9%) equipped with a dip tube was purchased from BOC Ltd., UK. All chemicals were used without further pre-treatment or purification.

2.2 Preparation and characterisation of lanthana-ceria-zirconia/graphene inorganic nanocomposite synthesis via CHFS

CHFS experiments were conducted using a reactor, basic design that has been reported elsewhere [11]. CHFS reactor consists of three high-performance pressure pumps used for the delivery aqueous solution of reagents. The catalyst was successfully prepared and characterised by Adeleye et al.,[8]. The properties of the prepared lanthana-ceria-zirconia/graphene inorganic nanocomposite catalyst *via* CHFS are given in Table 1.

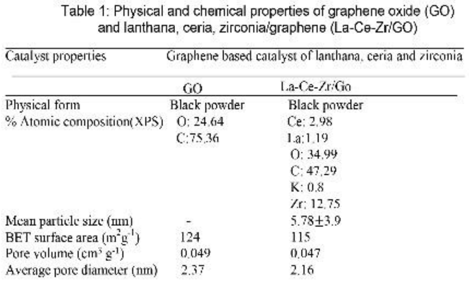


Table 1: Physical and chemical properties of graphene oxide (GO) and lanthana, ceria, zirconia/graphene (La-Ce-Zr/GO)

Catalyst properties	Graphene based catalyst of lanthana, ceria and zirconia	
	GO	La-Ce-Zr/Go
Physical form	Black powder	Black powder
% Atomic composition(XPS)	O: 24.64 C:75.36	Ce: 2.98 La:1.19 O: 34.99 C: 47.29 K: 0.8 Zr: 12.75
Mean particle size (nm)	-	5.78±3.9
BET surface area (m^2g^{-1})	124	115
Pore volume ($cm^3 g^{-1}$)	0.049	0.047
Average pore diameter (nm)	2.37	2.16

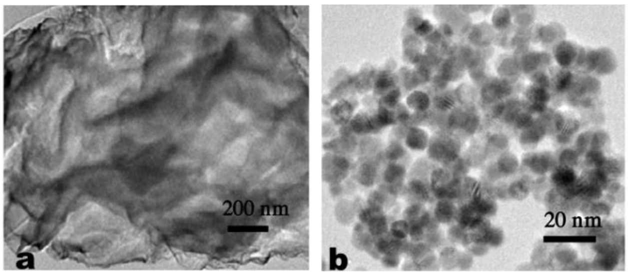


Figure 1. Transmission electron microscopy (TEM) images of graphene oxide and La-Ce-Zr/GO catalyst assessed for the synthesis of butylene carbonate (a) graphene oxide and (b) La-Ce-Zr/GO as prepared via CHFS.

2.3 Experimental procedure for the synthesis of butylene carbonate (BC)

The synthesis of BC was carried out in a 25 mL stainless steel high-pressure reactor equipped with a stirrer, thermocouple and a heating mantle and controller as shown in Figure 2. The reactor was charged with a required amount of BO and catalyst. The reactor was heated to the required temperature and continuously stirred at a known stirring speed. The supercritical fluid pump was used to pump CO_2 at a desired pressure from the cylinder to the reactor and left for a specified time. After the reaction, the reactor was cooled down to room temperature using an ice bath. The reactor was depressurised and the reaction mixture was filtered. The recovered catalyst was washed with acetone and dried in an oven while the products were analysed using a gas chromatography (GC) equipped with a flame ionization detector (FID) with a capillary column using octane as an internal standard. The effect of various parameters such as catalyst loading, CO_2 pressure, reaction temperature and reaction time were studied for the optimisation of the reaction conditions. Catalyst reusability studies were also conducted to assess the stability of the catalyst for synthesis of BC.

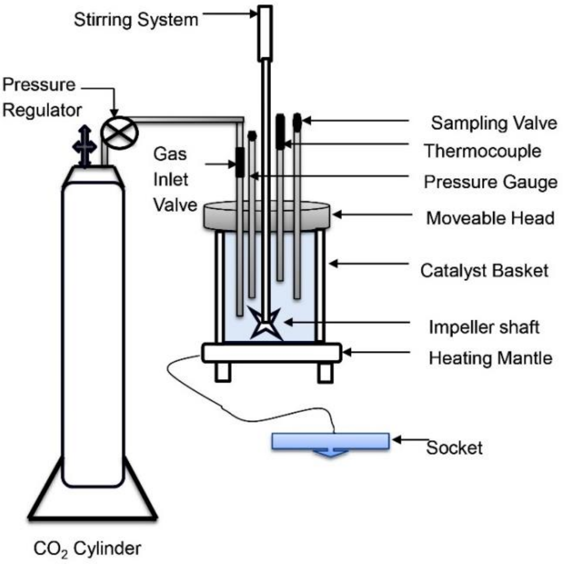
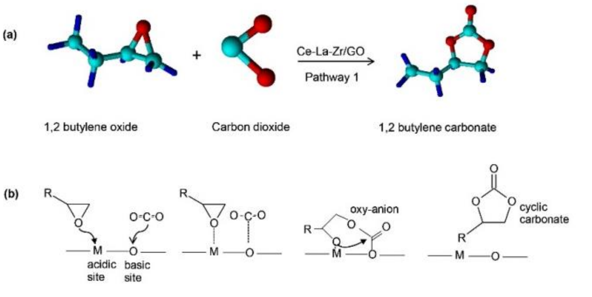


Figure 2. Schematic of a high-pressure reactor.

3.0 RESULTS AND DISCUSSION

3.1 Proposed reaction mechanism

The synthesis of BC through cycloaddition reaction of CO_2 to BO in the presence of La-Ce-Zr/GO inorganic nanocomposite catalyst can be seen in Figure 3a and 3b [12].



R stands for alkyl group, MO represents metal oxide catalyst, where M is a metal atom and O is an oxygen atom.

Figure 3. Reaction scheme and pathway for synthesis of butylene carbonate.

3.2 Effect of Reaction Temperature

The cycloaddition reaction of CO_2 to BO was carried out at several reaction temperatures ranging from 368 K to 443 K in order to study its effect on BO conversion and BC yield as well as its selectivity. In this study, the reaction conditions were set at 10% catalyst loading, 75 bar CO_2 pressure, and duration for 20 h. As it was expected, the higher the temperature, the more the conversion of butylene oxide into carbonates isomers and oligomers. Figure 4 shows the temperature dependence on the yield and selectivity of butylene carbonate.

In Figure 4 it was noticeable that there was a corresponding increase in conversion of BO, BC yield, and selectivity as a result of temperature increase from 368 K to 408 K but further increase of temperature from 408 K to 443 K, resulted in slight drop of butylene carbonate yield from 64% to 60%, whilst butylene oxide conversion increases from 84% to 90%.

The drop in the yield of BC and further conversion of BO could be as a result of partial decomposition of the product that resulted to the formation of oligomers which was also suggested by Adeleye et al.,[8].

From these results, it can be concluded that the optimum temperature for this exothermic reaction is 408 K at reaction conditions of 75 bar, 10% catalyst loading and duration of 20 h. Accordingly, the resultant reaction temperature has been included within the variables affecting reaction responses and therefore, has been used for optimisation using BBD of RSM.

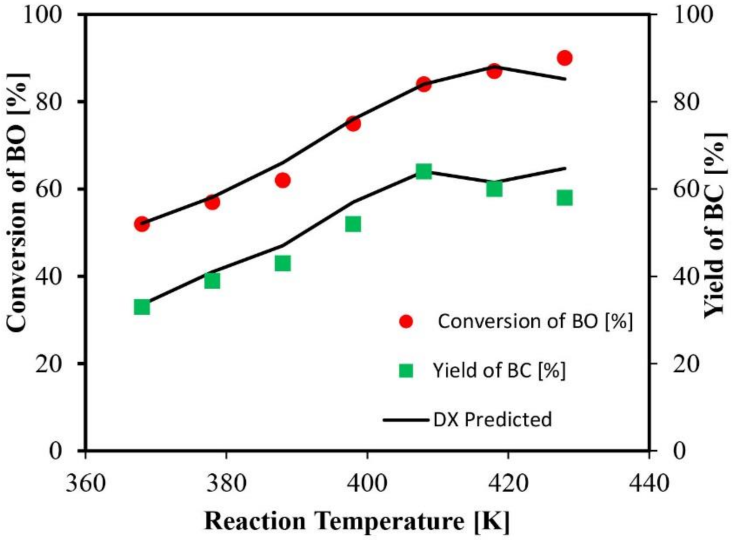


Figure 4. Effect of reaction temperature on conversion of BO and BC yield

3.3 Effect of CO_2 Pressure

The application of supercritical state of CO_2 reaction system is very significant for the synthesis of BC through the reaction of BO and CO_2. The use of CO_2 in the supercritical state can cause an increase in mass transfer efficiency of the reactants and shift the reaction equilibrium to open up the thermodynamic limitation of this reaction [13,14]. The effect of CO_2 pressure on BO conversion and BC yield was studied in order to establish the optimum CO_2 pressure for the cycloaddition reaction of CO_2 to BO. The experiments were carried out in a high-pressure reactor at 408 K with CO_2 pressure ranging from 55 bar to 105 bar for 20 h and the results are shown in Figure 5. As it was expected in Figure 5, an increase in CO_2 pressure from 55 bar to 75 bar increases BO conversion and the yield of BC, but beyond 75 bar there were further increase in BO conversion but no significant increase in the yield of BC rather an insignificant decrease in the yield.

At 75 bar of CO_2 pressure, BO conversion and BC yield were of 84% and 64% respectively. Beyond 75 bar, there was a slight drop in BC yield and that might be as a result of decomposition of BC to form oligomers. Therefore, it can be concluded that the optimum CO_2 pressure for this reaction is 75 bar. This study has shown an improvement in polarity and solubility of BO conversion at the supercritical condition of CO_2 as the reaction pressure increases. The use of BBD from RSM has been used to identify significant variables affecting reaction responses and optimise the resultant CO_2 pressure of the reaction.

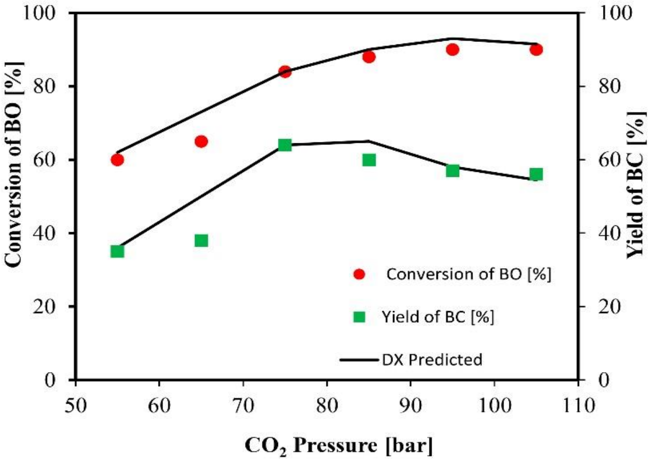


Figure 6. Effect of CO_2 pressure on conversion of BO and BC yield

3.4 Model Development and Adequacy Checking

The responses for each randomised experiments in terms of BO conversion and BC yield have been reported in Table 2. It has been observed from the experimental runs that BO conversion ranges from 42 to 90% while BC yield ranges from 16 to 65%. The variations within the wide range of both responses have shown their significant effect with respect to reaction variables. Multiple regression analysis of the experimental data has been performed using Design Expert software. It has generated two polynomial regression equations for each response variable representing an empirical relationship between reaction variables and each response variable as shown in Equations (1) and (2).

Table 2. Experimental design matrix with the actual and predicted responses.

Run	A: Temperature K	B: Pressure bar	C: Catalyst Loading w/w	D: Time h	Actual Conversion %	Y1: Predicted Conversion %	Actual Yield %	Y2: Predicted Yield %
1	170	75	15	20	86	87.96	64	64.38
2	135	75	10	20	84	84.00	64	64.00
3	135	90	10	24	90	97.29	65	66.04
4	135	75	15	16	69	67.83	35	35.46
5	100	75	5	20	54	55.79	23	24.88
6	135	60	10	24	75	72.96	40	41.04
7	135	90	10	16	70	75.79	35	36.21
8	135	60	5	20	66	58.88	37	33.50
9	100	60	10	20	42	46.33	16	14.63
10	135	60	10	16	68	64.46	35	36.21
11	135	90	15	20	88	91.38	65	66.50
12	135	75	5	24	67	68.17	33	32.29
13	135	90	5	20	86	81.21	36	35.00
14	135	60	15	20	77	78.04	44	43.00
15	135	75	10	20	84	84.00	64	64.00
16	170	90	10	20	86	81.67	45	46.13
17	135	75	15	24	89	85.33	65	64.29
18	170	75	5	20	54	59.29	26	28.88
19	170	75	10	16	68	62.38	38	33.33
20	100	75	15	20	58	56.46	31	30.38
21	100	75	10	16	52	52.88	23	24.33
22	170	75	10	24	90	85.38	64	60.67
23	135	75	10	20	84	84.00	64	64.00
24	100	75	10	24	58	59.88	29	31.67
25	100	90	10	20	90	82.67	55	51.13
26	135	75	10	20	84	84.00	64	64.00
27	170	60	10	20	75	82.33	54	57.63
28	135	75	10	20	84	84.00	64	64.00
29	135	75	5	16	52	55.67	26	26.46

$$Y1 = 84.00 + 8.75\,A + 8.92\,B + 7.33\,C + 7.50\,D - 9.25\,AB + 7.00\,AC + 4.00\,AD - 2.25\,BC + 3.25\,BD + 1.25\,CD - 11.63\,A^2 - 0.87\,B^2 - 7.50\,C^2 - 7.25\,D^2 \quad (1)$$

$$Y2 = 64.00 + 9.50\,A + 6.25\,B + 10.25\,C + 8.67\,D - 12.00\,AB + 7.50\,AC + 5.00\,AD + 5.50\,BC + 6.25\,BD + 5.75\,CD - 14.50\,A^2 - 7.13\,B^2 - 12.38\,C^2 - 12.00\,D^2 \quad (2)$$

Where, Y1, Y2 represent response variables including BO conversion and BC yield, respectively. A, B, C, and D represent independent variables including; temperature, pressure, catalyst loading and time, respectively. The predicted RSM models have been examined for adequacy to report the possible problems associated with the normality assumptions. The RSM models have been validated by ANOVA at 95% confidence level. Fisher's F-test and p-value have been used to determine the significance of the corresponding variable. Equations (1) and (2) have concluded a good visualisation of the effect of significant variables and their interaction on each response. High values of determination coefficients (R2 of 0.957 and 0.975 for both BO conversion and BC yield models, respectively. These results show good correlation between actual and predicted results. These results indicate that only 0.013 and 0.005 of the total variation have not been well clarified for BO conversion and BC yield, respectively, which indicates very high fitting of the predicted models with the experimental data. The ANOVA for both developed models has been applied to examine the significance of the model for fitting the experimental data.

Table 3. Analysis of variance (ANOVA) for response surface developed a model

	Sum of Squares		Mean Squares		F-values		p-values	
Source	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2	Y_1	Y_2
Model	5194.09	7446.55	371.01	531.90	11.31	68.68	2.57E-05	1.99E-10
A-Temperature	918.75	1083.00	918.75	1083.00	28.02	139.85	0.000114	1.13E-08
B-Pressure	954.08	468.75	954.08	468.75	29.10	60.53	9.46E-05	1.89E-06
C-Catalyst Loading	645.33	1260.75	645.33	1260.75	19.68	162.80	0.000564	4.24E-09
D-Time	675.00	901.33	675.00	901.33	20.58	116.39	0.000465	3.62E-08
AB	342.25	576.00	342.25	576.00	10.44	74.38	0.006041	5.65E-07
AC	196.00	225.00	196.00	225.00	5.98	29.05	0.028325	9.53E-05
AD	64.00	100.00	64.00	100.00	1.95	12.91	0.184153	0.002936
BC	20.25	121.00	20.25	121.00	0.62	15.62	0.445062	0.001444
BD	42.25	156.25	42.25	156.25	1.29	20.18	0.275397	0.000507
CD	6.25	132.25	6.25	132.25	0.19	17.08	0.669078	0.001016
A^2	876.59	1363.78	876.59	1363.78	26.73	176.11	0.000142	2.54E-09
B^2	4.97	329.29	4.97	329.29	0.15	42.52	0.703011	1.35E-05
C^2	364.86	993.34	364.86	993.34	11.13	128.27	0.004902	1.96E-08
D^2	340.95	934.05	340.95	934.05	10.40	120.62	0.006115	2.89E-08

Table 3 summarises the ANOVA results for both BO conversion and BC yield models. The significance of the model is determined at high Fisher's F-value and low probability p-value. Based on the ANOVA results for BO conversion (Y1), F-value and p-value have been reported by 68.69 and <0.0001, respectively. While for BC yield (Y2), F-value and p-value have been evaluated as 11.31 and <0.000026, respectively. These results indicate the quadratic developed model is highly statistically significant with 95% confidence level. A plot between predicted *versus* actual values showed reasonable agreement and high correlation. The efficient estimation of the response values is concluded from the similarity of both predicted and actual results of BO conversion and BC yield as shown in Figures 7 and 8, respectively. The predicted model's values have been applied to the previously determined OFAT experiments reported by Onyenkeadi et al.,[12] The similarity between predicted and actual experimental values at a wide range of a number of OFAT experiments proved the significance and adequacy of the predicted regression models.

3.5 Effect of Process Variables Interactions

From the results of ANOVA in Table 3, it could be stated that the first order process variables have shown a significant effect on process responses with a p-value lower than 0.05. It could be concluded that reaction pressure (B) is the most significant variable affecting BO conversion recording the highest F-value of 29.10. Similarly, catalyst loading (C) has been concluded as the most significant variable affecting BC yield with F-value of 162.80. These results have been confirmed using analysis of response surface, which provide visualisation of the predicted model with three-dimensional plots. These plots illustrate the effect of process variables on the responses by varying two intendant variables and analyse their effect on each response while holding the other variables constant at their centre points.

The effect of reaction temperature and pressure is clearly shown in Figures 9 and 10 for BO conversion and BC yield, respectively. It is clearly shown in Figures 9 and 10 that both responses increase while increasing reaction temperature at low-pressure levels. However, at an increased pressure, the effect of temperature changes and the responses increase the temperature until specified temperature which starts to have a negative impact on the responses. These conclusions show the importance of analysing the effect of interaction between variables as it has been concluded from Figure 5 that the effect of temperature is directly proportional on both responses, however, this conclusion is only valid at constant pressure values as varying pressure with temperature has shown the different interactive effect on the responses. Similarly, the effect of reaction pressure on both responses is illustrated in Figures 9 and 10. At low temperatures, the pressure shows a direct linear relationship with reaction responses, while at higher temperature the responses behaviour changes with increasing reaction pressure. Figures 11 and 12 show the effect of catalyst loading and reaction time on both BO conversion and BC yield, respectively.

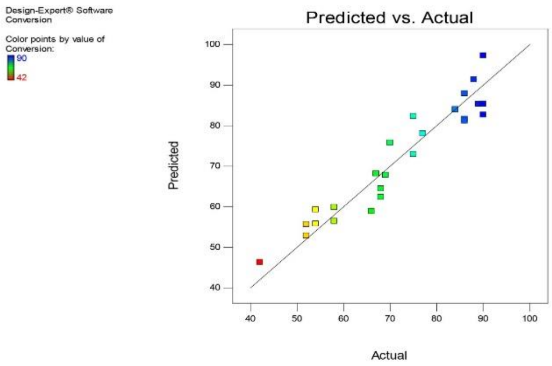


Figure 7. Actual experimental data *versus* predicted values for BO conversion

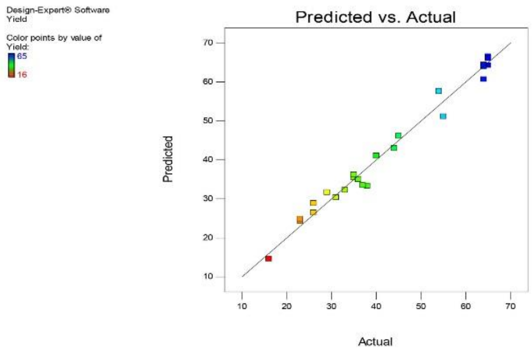


Figure 8. Actual experimental data *versus* predicted values for BC yield.

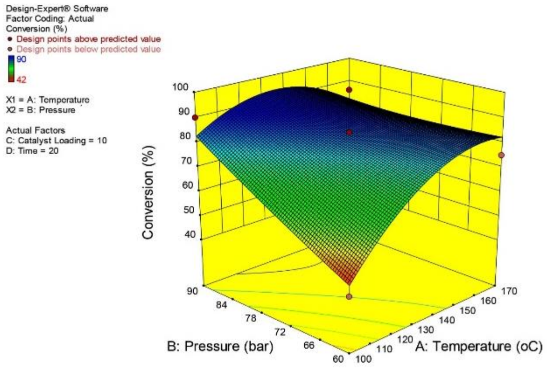


Figure 9. Response surface plot for the effect reaction temperature and pressure on BO conversion.

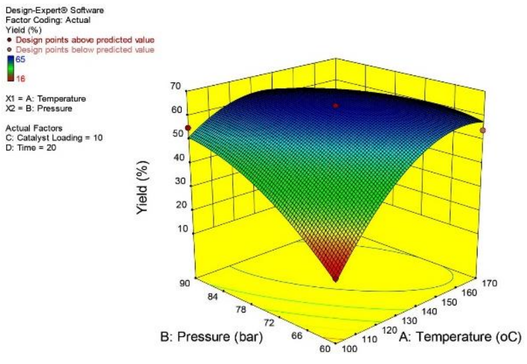


Figure 10. Response surface plot for the effect reaction temperature and pressure on BC yield.

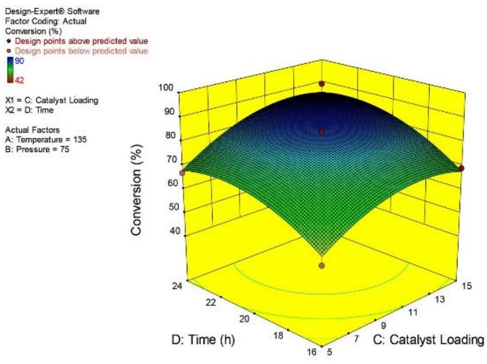


Figure 11. Response surface plot for the effect reaction catalyst loading and reaction time on BO conversion.

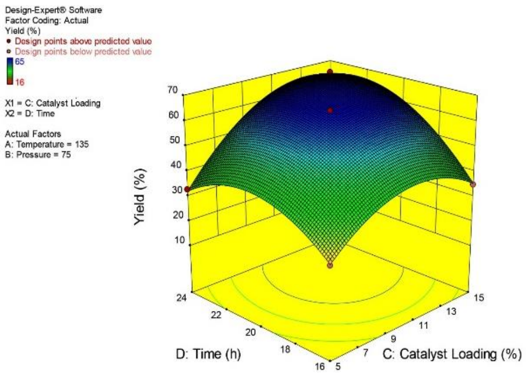


Figure 12. Response surface plot for the effect reaction catalyst loading and reaction time on BC

4.0 Conclusions

The synthesis of butylene carbonate through cycloaddition reaction of carbon dioxide and butylene oxide was successfully carried out using a high-pressure reactor in the presence of various heterogeneous catalysts without any organic solvent. Among the used heterogeneous catalysts ceria, lanthana, zirconia/graphene inorganic nanocomposite catalyst (Ce-La-Zr/GO) was found to be the best-performed catalyst and the optimum reaction condition was found at 408 K, 75 bar CO_2 pressure, 10% (w/w) catalyst loading, and 20 h reaction. RSM using BBD has been used to develop regression models representing BO conversion and BC yield in the established significant process variables. The reaction temperature, pressure, time and catalyst loading have been determined as the significant variables affecting reaction responses using OFAT method. It has been established that the optimum reaction conditions using OFAT method at 408 K, 75 bar, 10% (w/w) catalyst loading in 20 h reaction time gave a conversion of BO and BC yield of 84 % and 64 %, respectively. However, using RSM numerical optimization the optimum conditions have been found to be 140 K, 82 bar, 9% (w/w) catalyst loading in 22 h reaction time and gave BO conversion of 90% and BC yield of 65%. The predicted optimum conditions have been validated experimentally with 1.45% and 1.52% relative error for both BO conversion and BC yield, respectively.

5.0 References

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