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ANOVA Analysis for Bio-Oil Upgrading by Catalytic Cracking

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Abstract: Environmental issues and the security of energy supply have stimulated interest in the development of alternatives for fossil based energy carriers and chemicals. Biomass has been identified as a promising resource because it is abundantly available and in principle CO_2 neutral. Upgradation of bio-oil before utilization is desirable to obtain high grade fuel. This study focuses on the ANOVA analysis of effective parameters for upgrading bio-oil by catalytic cracking with Response Surface Methodology (RSM). Second order quadratic model is predicted by statistical analysis and shows that experimental values are best fitted. The p-value for yield and Degree Of Deoxygenation (DOD) is 0.0001 which indicates that predicted model is significant for both response factors. Lack of fit for yield and DOD is 0.4829 and 0.5553, respectively. The coefficient of determination for yield and DOD is 0.9821 and 0.9844, respectively which indicates that experimental data is best fitted into predicted model. Actual versus predicted values plot implies that the difference between experimental values for yield and DOD is insignificant.

Key words: Catalytic cracking, bio-oil, response surface methodology

INTRODUCTION

Due to the continuous increase in population and industrialization, energy consumption is increasing but energy sources are decreasing (Crocker and Andrews, 2010; Luque *et al*., 2010). Most of the developing countries are facing two major problems related to fossil fuel such as emissions and the limited resources (Peters, 2003). Due to the burning of fossil fuels SOx and NOx are emitted which are the major cause of acid rain and greenhouse gas that posed major threat to world climate (Satterfield, 1991; Zhang *et al*., 2006). If this phenomenon continues, it is forecasted that some extreme natural calamities are expected.

Biomass is being considered to be an efficient alternative energy resource via converting it to liquid product in high heating process named as pyrolysis (Mohan *et al*., 2006). Vapors produced by pyrolysis of biomass are condensed to a liquid product known as bio-oil that has dark brown color and pungent smell (Xiu and Shahbazi, 2012). Bio-oil or pyrolysis oil has the potential to be used as an alternative to fossil fuel (Zhang *et al*., 2007; Xu *et al*., 2011). Crude bio-oil can be used directly in boilers, different important chemicals can be separated from it and it can also be upgraded so that it can be used in engines for energy generation (Gopakumar, 2012). Bio-oil contains large amount of oxygen almost 35-40 wt% (Zhang *et al*., 2007) and can be decomposed to release oxygen as H_2O, CO_2 or CO in the presence of catalyst to form hydrocarbon (Williams and Horne, 1994).

Catalytic upgrading of bio-oil is an essential process to convert it into refined fuels that can be used directly for transportation or it become miscible with existing petroleum fractions (gasoline, diesel and kerosene) (Hew *et al*., 2010; Mortensen *et al*., 2011; Park *et al*., 2011). Hydrodeoxygenation and catalytic cracking are considered as two main ways to convert oxygenated bio-oil into pure hydrocarbon fuels (Pindoria *et al*., 1998). Compared with hydrodeoxygenation, catalytic cracking converts bio-oil into pure hydrocarbon fuels without hydrogen consumption which makes it more economical (Pindoria *et al*., 1997; Guo *et al*., 2011a). The catalytic cracking of crude bio-oil has been ongoing for long time and some achievements in decreasing oxygen content and conversion of bio-oil into hydrocarbons have been made but the reasons for catalyst deactivation in cracking of crude bio-oil have not been completely revealed (Vitolo *et al*., 1999; Guo *et al*., 2011b).

In most of the earlier report on batch and continuous mode studies, effect of individual parameters has been reported while maintaining other process parameters constant at unspecified levels. This approach does not depict the combined effect of all process parameters. It is time consuming and requires a number of experiments to

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determine optimum levels which may be unreliable. These limitations of a classical method can be eliminated by considering all the process parameters collectively by statistical experimental design such as Response Surface Methodology (RSM) (Tamunaidu and Bphatia, 2007; Ellens and Brown, 2012). The present study focus on statistical analysis by ANOVA for yield and maximum bio-oil deoxygenation in a laboratory-scale fixed bed reactor using a central composite design of experiments with temperature range from 300-500°C, pressure 0.1-0.3 MPa and oil to catalyst ratio from 15-30.

MATERIALS AND METHODS

Bio-oil: Model bio-oil samples were freshly prepared before each experiment and consisted of acetic acid (10 wt%), 2-furaldehyde (20 wt%), acetone (10 wt%), phenol (30 wt%) and water (30 wt%).

Catalyst: Commercially available catalyst HZSM-5 is being used in this process with SiO_2/Al_2O_3 ratio of 30 with the surface area of 400 $m^2 g^{-1}$. The catalyst is purchased from Zeolyste International USA and it is in H-exchanged form.

Fixed bed reactor: All the experiments were conducted in fixed bed reactor. Initially, the reactor was loaded with 3 g of catalyst on glass wool supported by wired fixed bed and the upper surface of the catalyst is again covered by glass wool. The reactor was therefore placed in a furnace. The reactor was heated to desired temperature and purged continuously with N_2 gas (50 mL min^{-1}) until desired temperature and pressure conditions are achieved. Subsequently, the bio-oil was pumped into the reactor with constant flow rate of 1 mL min^{-1}. Finally, the condensed liquid products were collected at the outlet of condenser while gaseous products were collected in gas tank. Thereafter, both collected products were subjected to GC analysis.

Two performance indicators calculated that include, oil yield and degree of de-oxygenation:

$$Y_{oil}\ (\%) = \left(\frac{m_{oil}}{m_{feed}}\right)\times 100 \quad (1)$$

$$DOD\ (\%) = \left(1-\frac{\text{wt\%o in product}}{\text{wt\%o in feed}}\right)\times 100 \quad (2)$$

where, Y_{oil} is the yield of oil, m_{oil} is the weight of produced oil, m_{feed} is the weight of feed, DOD is the degree of de-oxygenation and wt%o is weight percent of oxygen in oil. These two parameters give an overview of the extent of reaction.

Statistical analysis: Yield and degree of deoxygenation DOD of upgraded liquid were modeled with formulae second order polynomials:

$$y = \beta_0 + \sum_{i=1}^{k}\beta_{ii}x_i + \sum_{i=1}^{k}\beta_{ii}x_i^2 + \sum i = 1\sum j = i+1\beta_{ii}x_{ij} + \in \quad (3)$$

where, y is the model response, β_0 is the intercept constant, β_i, β_{ij} and β_{ii} are model coefficients, x_i, x_ix_j and x_i^2 are coded single terms, interaction terms and quadratic terms, respectively.

The analysis of variance (ANOVA), lack of fit and coefficients from each yield and DOD model were analyzed for significance. Parameters with p-values less than 0.05 were considered significant with 95% confidence. Full quadratic models were reduced to only those terms that were statistically significant which greatly simplified the models. The coefficient of determination or R^2 value was assessed as an indication of how well the model fit the data and how much variability in the data could be described by the model. Lack of fit was assessed to ensure that the quadratic model was the most appropriate model type.

RESULTS AND DISCUSSION

Response Surface Methodology (RSM) approach is used to study the effect of three process variables i.e. temperature, pressure and oil to catalyst ratio on the yield of Organic Liquid Product (OLP) and Degree Of Deoxygenation (DOD). Yield of Organic Liquid Product (OLP) and degree of deoxygenation are taken as response variables. The 20 runs are obtained by using Design Expert 8.0 software by using central composite design CCD based on RSM approach. The experiments were performed on set conditions of process variables. Both response factors yield and DOD of OLP are calculated for each run. Table 1 contains all values of response variables, yield and DOD of OLP at all process operating conditions. The main aim for using experimental design is to obtain the process conditions which give the yield of OLP that contains least amount of oxygen among all. The response variables such as degree of deoxygenation DOD increases from 7.65-45.65 and for yield it decreases from 74.45-61.08 wt%.

ANOVA analysis for yield of OLP: Linear multiple regression program of the design expert software is used to derive a relation between the independent variables (temperature, oil/catalyst ratio and pressure) and the response variable yield. The model predicted shows quadratic correlation and it is given as in Eq. 4:

Table 1: Experimental design with response variables

Run	Temperature (°C)	Oil/catalyst	Pressure (bar)	Yield (wt%)	DOD (%)
1	500	15.0	3	61.08	45.56
2	300	15.0	3	70.62	17.37
3	300	30.0	3	73.01	11.08
4	300	30.0	1	74.45	7.65
5	400	30.0	2	67.31	22.16
6	300	15.0	1	71.95	15.39
7	400	22.5	2	67.31	23.09
8	500	30.0	3	63.87	39.48
9	400	22.5	2	67.98	21.11
10	500	22.5	2	63.36	41.92
11	400	22.5	2	67.20	23.12
12	300	22.5	2	72.51	14.29
13	400	22.5	2	64.52	26.25
14	400	22.5	2	66.11	24.21
15	400	22.5	2	66.79	25.79
16	400	22.5	1	67.51	23.53
17	500	30.0	1	64.56	36.55
18	500	15.0	1	62.96	43.16
19	400	22.5	3	65.32	29.93
20	400	15.0	2	65.36	26.64

Table 2: ANOVA analyses for yield

Parameters	Source	F-value	p-value
Selected model	Model	61.01	0.0001
Process variables			
Temperature	A	494.45	0.0001
Oil/catalyst	B	24.09	0.0006
Pressure	C	12.85	0.0050
Temperature×oil/catalyst	AB	0.071	0.7956
Temperature×pressure	AC	0.011	0.9173
Oil/catalyst×pressure	BC	0.33	0.5781
Temperature^2	A^2	14.33	0.0036
(Oil/catalyst)^2	B^2	1.84	0.2046
Pressure^2	C^2	0.0082	0.9929
Model check	Lack of fit	1.04	0.4829

$$Y_{OLP} = 66.76-4.76A+1.03B-0.75C-0.062AB+0.025AC+0.14BC+1.52A^2+0.54B^2+3.36\times10^{-3}C^2 \quad (4)$$

where, A is temperature, B is oil/catalyst ratio and C is pressure. To verify the significance of the model, the experimental data is fitted into the predicted model different test are performed which involves the verification of each model coefficient and lack of fit test for the predicted model. This technique for verification of experimental data through statistical analysis is known as the analysis of variance ANOVA. In addition, this method can deduce the results of the system where several factors are effective and can be varied simultaneously as shown in Table 2. In order to check the significance of the model probability value p-value and F-value are taken as proof. For 95% confidence level the p-value should be less than 0.05 with high F-value. So, for the present study experimental data is best fitted into predicted model as it has p-value of 0.0001 which is very less than 0.05 and also poses high F-value as shown in Table 2. Another test for verifying the significance of model was to check "Lack of fit" and its F-value is 1.04 which indicates that lack of fit is not significant and there is 48.29% chance for model to

Table 3: Coefficient of determination of yield

Coefficients	Values
Determination coefficient (R^2)	0.9821
Adjusted determination coefficient (Adj R^2)	0.9661
Predicted determination coefficient (Pred R^2)	0.9201
Adequate determination coefficient (Adeq R^2)	27.485

the lack of fit to the experiment data. In order to fit the experimental data to the model non-significant lack is good. Moreover ANOVA can also be used to check the significance of individual independent process variables and the effect of their interaction within the model in addition to check its significance of the complete model. As stated earlier the model is for significance the p-value is less than 0.05. Based on Table 2 the significance of individual variables is checked, all process variables are significant. The p-value for temperature is 0.0001, oil/catalyst is 0.0006 and pressure it is 0.005. Furthermore the p-value for temperature into oil/catalyst, temperature into pressure and pressure into oil/catalyst are 0.7956, 0.9173 and 0.5781, respectively which lies in the range of marginal significance (0.05<p-value<0.1). In case of squared process variables temperature is significant give the p-value is 0.0036 while oil/catalyst ratio and pressure p-value is 0.5046 and 0.9929, respectively and lies within the marginal range (0.05<p-value<0.1).

Table 3 shows the determination coefficient (R^2), Adjusted determination coefficient (Adj R^2), Predicted determination coefficient (Pred R^2) and Adequate determination coefficient (Adeq R^2). The value of determination coefficient for current model is 0.9821 which indicates that the experimental data is fitted into model with 98.21% accuracy. While it has been reported by several researchers that by increasing the number of operating variables the value of determination of coefficient increases to over this two new terms are

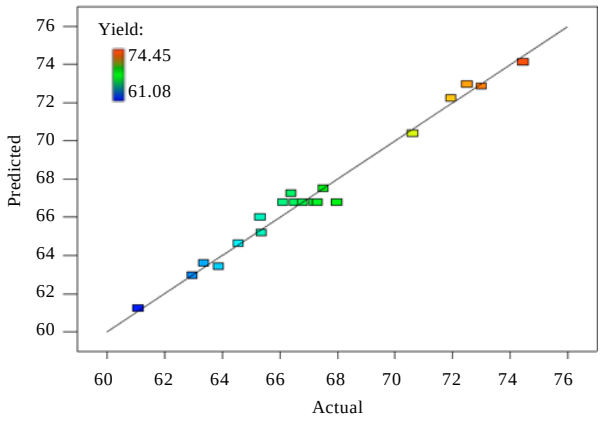

Fig. 1: Actual versus predicted values plot for yield

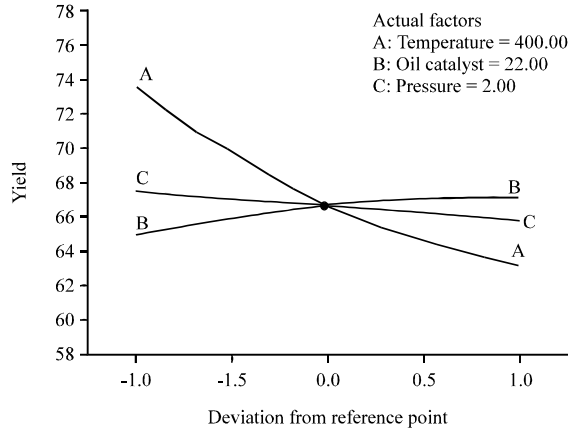

Fig. 2: Perturbation plot for yield

introduced by ANOVA such as Adj R^2 and Pred R^2. Both Adj R^2 and Pred R^2 have values of 0.9661 and 0.9201, respectively which shows good agreement between each other. The most important portion of the data analysis is to verify the adequacy of model and it is 27.485, i.e., greater than 4 which implied that the model is adequate to represent the experimental data.

Predicted versus actual values for yield of OLP: Figure 1 shows the plot between experimental versus predicted value. After verifying the significance of predicted model by statistical analysis based on the experimental data, this model can be used to calculate the theoretical value of response variable yield. From Fig. 1, it can be seen that experimental values are best fitted into predicted model. Only few points vary from the central line while majority of points lies into the central region. It is observed that majority of points indicating the yield in wt% lies within the range of 66-73 wt% and it is considered most populated area. The minimum value of yield is 61.08 wt% and goes to 74.5 wt% by changing the operating conditions. For the current process it is not required to get the maximum yield but it is to obtain the value of yield on which degree of deoxygenation is maximum.

Table 4: ANOVA analysis for DOD

Parameters	Source	F-value	p-value
Selected model	Model	69.89	0.0001
Process variables			
Temperature	A	579.81	0.0001
Oil/catalyst	B	28.43	0.0003
Pressure	C	8.58	0.0151
Temperature×oil/catalyst	AB	0.066	0.8031
Temperature×pressure	AC	0.0023	0.9881
Oil/catalyst×pressure	BC	0.14	0.7131
Temperature^2	A^2	5.41	0.0423
(Oil/catalyst)^2	B^2	0.99	0.3435
Pressure^2	C^2	1.20	0.2997
Model check	Lack of fit	0.88	0.5553

Perturbation: Perturbation is basically the method which belongs to linear approximation. This approach takes higher order terms into account for approximation. From the perturbation plot in Fig. 2, we can judge the influence of each variable while other variables are assumed constant. The plot indicates that the most influencing variable on the yield is temperature as it causes rapid decrease in yield compared to that of pressure and oil/catalyst ratio. Oil/catalyst ratio curve in perturbation graph shows that it is second most affecting variable to yield. Pressure also affects yield but it imposes the least impact compared to the other two variables.

ANOVA analysis for DOD of OLP: Similarly ANOVA is applied to check the significance of model and its suitability. The quadratic model for DOD in terms of the coded factors given by the software is shown in Eq. 5:

$$DOD = 24.56+14.09A-3.12B+1.71C+0.17AB-10^{-2}AC+ 0.25BC+2.6A^2-1.11B^2+1.22C^2 \quad (5)$$

where, A is temperature, B is oil/catalyst ratio and C is pressure. In order to check the significance of model we have look upon the results generated by ANOVA. While based on this analysis of variance results significance of each coefficient and lack of fit is analyzed. Model selected for DOD is significant and this is judged from its p-value 0.0001 as it should be less than 0.05 with high F-value of 69.89. From Table 4 it can be observed that process temperature is the most significant factor as the F-value is 579.81 and highest among others. The second test for the verification of selected model is significant or

Table 5: Coefficient of determination for DOD

Coefficients	Values
Determination coefficient (R^2)	0.9844
Adjusted determination coefficient (Adj R^2)	0.9703
Predicted determination coefficient (Pred R^2)	0.9453
Adequate determination coefficient (Adeq R^2)	28.927

is to check the model's "Lack of fit". According to ANOVA results for lack of fit using F-value of 0.88 which is not significant while it's p-value is 0.553. The p-value for lack of fit indicates that there is only 55.57% chance that a "Lack of fit F-value" this large could occur due to noise. Furthermore non-significant "Lack of fit" is good for experimental data to fit in predicted model. While in terms of significance of individual parameter the temperature, oil/catalyst and pressure are all significant as their p-values are 0.0001, 0.0003 and 0.0151, respectively the F-value for the temperature is 579.81, oil/catalyst 28.43 and pressure has least 8.58. Moreover, the p-value of temperature into oil/catalyst is 0.8031, for temperature into pressure is 0.9881 and oil/catalyst into pressure is 0.7131 which all are greater than 0.05 which means that they are not significant. While for square of temperature the p-value is 0.0423 which indicates its significance meanwhile square of oil/catalyst and pressure is not significant which has p-value 0.3435 and 0.2997, respectively.

Table 5 contains the value of determination coefficient (R^2), Adjusted determination coefficient Adj R^2, Predicted determination coefficient (Pred R^2) and Adequate determination coefficient (Adeq R^2). The value of R^2 is 0.9844 indicates that with the accuracy of 98.44% the experimental data is fitted into the predicted model. Adj R^2 and Pred R^2 are 0.9703 and 0.9453, respectively and have reasonable agreement between each other. In order to check the adequacy of model adequate determination coefficient is calculated and its value should not exceed 4 for the current study the adequate determination coefficient is 28.927.

Experimental versus predicted plot for DOD: Figure 3 illustrates the plot between actual versus predicted value of degree of deoxygenation from catalytic cracking of model bio-oil in lab scale catalytic cracking unit. From Fig. 3 it can be seen that only few points of degree of deoxygenation experimentally obtained varies from center line. The observation from plot led to explanation that experimentally obtained data is best fitted into the quadratic model predicted by software. So, from this quadratic model one can predict the degree of deoxygenation at different points. The degree of deoxygenation for the present study varies from 7.65-45.56% and majority of points lies within the range of 15-31%. For the current study the aim is to obtain the maximum degree of deoxygenation and it is 45.65% of organic liquid product is obtained.

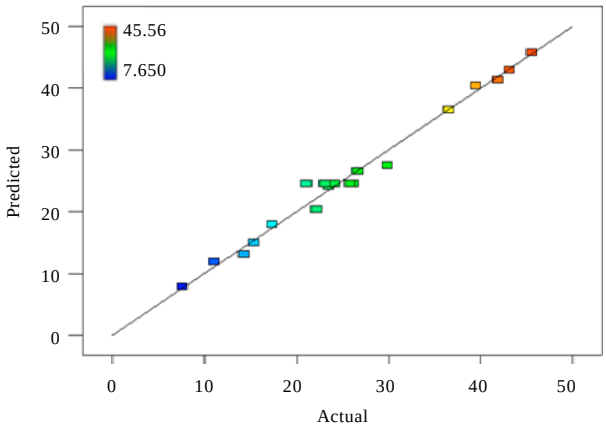

Fig. 3: Actual versus predicted values plot for DOD

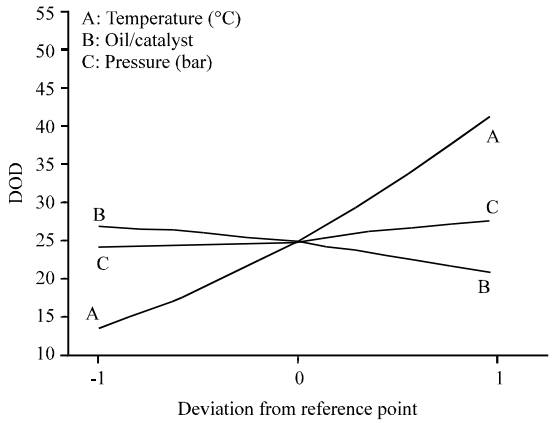

Fig. 4: Perturbation plot for DOD

Perturbation: From the perturbation plot in Fig. 4, it can be observed that most influencing factor on the liquid product DOD is the process temperature as it gives the steepest curve. The effect of each factor is pondered by keeping the other variables constant. Perturbation plot can be helpful in product selectivity in case some products are temperature sensitive. Meanwhile, due to temperature the chains of organic compounds cause the oxygen from attached within them to be released and caused them to form hydrocarbons. Furthermore oil/catalyst ratio is also an influencing factor for degree of deoxygenation but if compared to temperature, the influence of oil/catalyst is less. Pressure is the least affecting variable as indicated by the plot.

CONCLUSION

The high F-value of 68.89 and low p-value of 0.0001 of the predicted model for yield proved its significance. Determination of coefficient for yield and DOD of

upgraded liquid product shows 98.21% accuracy for process parameters selected are effective for catalytic cracking. Perturbation plot exhibits that the most effective parameter for catalytic cracking is temperature.

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