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Optimization and Characterization of Ethyl Ethanoate Produced from Cellulosic Bioethanol using an Organic Acid

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Abstract: *This research presents the report of the optimization of the esterification process using* 2^4 *factorial designs to study the effects of temperature (A), the mole ratio of bioethanol to ethanoic acid (B), catalyst concentration (C) and esterification time (D) on the yield of ethyl ethanoate. A maximum yield of* 98% *of ethyl ethanoate was obtained at the temperature of* 65 ℃, *the mole ratio of bioethanol to ethanoic acid of* 2: 1, *catalyst concentration of* 0.25 $wt\%$ *and esterification time of* 90 $minutes$. *Design expert software utilized in the statistical analysis of* 2^4 *factorial designs indicates that esterification time and the temperature had the highest effect of 58.50 and 17 respectively. The model equation developed was given as* $Yield = 58.00 + 8.50A - 3.13B - 1.75C + 29.25D - 0.38AB + 0.00AC - 0.50AD + 0.36BC + 0.87BD + 0.50CD - 0.12ABC + 0.88ABD + 0.50ACD - 0.12BCD + 0.12ABCD$. *Characterization results of ethyl ethanoate revealed that kinematic viscosity, specific gravity, flash point, refractive index, sulphur content and water content agreed with the ASTM standard. The FT-IR of the ethyl ethanoate samples indicated the characteristic functional groups peculiar with ethyl ethanoate. Overall, the produced ethyl ethanoate from cellulosic bioethanol possessed the required properties compared with the standard.*

Keywords: *Esterification, factorial design, bioethanol, ethanoic acid, ethyl ethanoate*

INTRODUCTION

Esters are chemical compounds with a characteristic sweet smell, flavours and aromas. The chemical structure of esters is $R - COOR^1$, where R is the alkyl group and R^1 is the aryl group. It has been reported that the most universal method of ester production is via the application of heat to a carboxylic acid, $R - COOH$ with alcohol, $R - OH$ in the presence of a homogenous catalyst (Hangx *et al.*, 2001). The bioethanol produced from biomass such as cassava peels can be converted into ester via esterification process which is the reaction between an organic base and an organic acid to form an ester and water with bioethanol as an organic base and ethanoic acid as an organic acid (Nada *et al.*, 2010). The reaction between cellulosic bioethanol and ethanoic acid is slow and reversible at room temperature (Katz, 2006).

Tetraoxosulphate (VI) acid is used as a catalyst in the reaction between bioethanol and ethanoic acid to yield ethyl ethanoate as an ester and water (Katz, 2006) with the removal of water formed from the reaction mixture through distillation to enhance the production of ethyl ethanoate. According to Neil (2004), the rate of esterification reaction is enhanced with the aid of a homogenous catalyst because the limiting step in the esterification reaction mechanism is the protonation of the carboxylic acid. The esterification reaction is reversible with ester formed in the forward reaction and the hydrolysis of ester occurs in the backward reaction. However, some esters occur naturally as vegetable oils, palm oil, castor oil, groundnut oil, olive oil and animal fats (Katz, 2006). Esters are a colourless, volatile liquid with a characteristic smell that is slightly soluble in water and boils at 77 °C. Chemically, ester undergoes hydrolysis, reduction, reaction with amine and burns with a bright flame (Jumoke, 2005). Esters are used in flavouring essences, perfumes and as solvents for substances like paints, nail varnishes and cellulose (Hamelinck, 2004).

Calver *et al*. (2007) and Ismail *et al*. (2001) have investigated the production of ethyl ethanoate through the esterification of ethanoic acid and ethanol, but only covers limited temperature range and the mole ratio of ethanoic acid to ethanol. Nada *et al*. (2010) reported that the relationship between the mole ratio of ethanol to ethanoic acid is limited in the literature. The previous studies have limited information on the interactions between the process variables of temperature, the mole ratio of ethanol to ethanoic acid, catalyst concentration and esterification time towards achieving a high-quality ester production. This present study is required to determine the optimal conditions of process parameters such as temperature, the mole ratio of bioethanol to ethanoic acid, catalyst concentrations and time for esterification processes of converting cellulosic bioethanol from cassava peel to ethyl ethanoate. These conditions are very important to optimize the above process for optimum ester production. Hence, the production of ethyl ethanoate from cellulosic bioethanol will provide a viable route for the production of protic solvents for a wide range of industrial applications.

MATERIALS AND METHODS

2.1 Materials

The chemicals utilized for the esterification process are of analytical grades (95-99.5 %). The chemicals include ethanoic acid (BDH, England), Sulphuric acid (BDH, England) and bioethanol. The equipment used are Abbe refractometer (Gallenkamp, England), digital weighing balance (Citizen, India), Steam distillation set up (Setastill, Germany), distillation flask (Pyrex, England), Erlenmeyer/conical flask (Pyrex, England), flash point tester, flat bottom flask (Argonne, USA), funnel (OK plastic, Nigeria), hydrometer (Pyrex, England), magnetic stirrer (Gallenkamp, England), magnetic heater (Gallenkamp, England), measuring cylinders (Pyrex, England), distillation tube (Pyrex, England), oven (Stanhope seta), sulphur analyser (Horea SLFA-2800), thermometer (Pyrex, England), water bath (Stanhope seta), vacuum pump, viscometer (Stanhope seta), viscometer bath (Stanhope seta) and viscometer holder (Stanhope seta). The bioethanol used in this study was obtained from previous work reported elsewhere (Egbosiuba *et al*., 2014).

2.2 Production of Ethyl Ethanoate

The production of ethyl ethanoate was made feasible through the an esterification reaction of bioethanol and ethanoic acid. The experiment was performed using the factorial design method of analysis. Temperature, the mole ratio of bioethanol to ethanoic acid, catalyst concentration and reaction time were varied using 2^4 factorial design matrix method. The experimental set-up consists of steam distillation apparatus using a 250 mL of distillation tube with an opening for the thermometer. The distillation tube serves as a batch reactor and the arrangement was built up with a reflux condenser to prevent any loss of products.

As shown in run 1 of Table 1, a calibrated beaker was used to measure 100 mL of the ethanol and ethanoic acid solution in the ratio of 2:1 into the distillation tube of the distillation set up with the aid of a funnel. Dilute tetraoxosulphate (VI) acid of 0.25 wt% was added to the reaction mixture in the distillation tube. The reaction mixture was efficiently stirred to avoid the reaction of the acid to form unwanted by-products. The reaction vessel was kept constant at 35 °C with the aid of the thermostatic heater and the thermometer. A conical flask was placed at the outlet point of the upper arm of the condenser for the collection of the ethyl ethanoate as the distillate.

Table-1 Experimental Matrix for the 2^4 Factorial Design Technique

Run	Temperature (°C)	Mole ratio (g/mol)	Catalyst Concentration (wt%)	Time (minutes)
1	35	2:1	0.25	30
2	65	2:1	0.25	30
3	35	4:1	0.25	30
4	65	4:1	0.25	30
5	35	2:1	0.5	30
6	65	2:1	0.5	30
7	35	4:1	0.5	30
8	65	4:1	0.5	30
9	35	2:1	0.25	90
10	65	2:1	0.25	90
11	35	4:1	0.25	90
12	65	4:1	0.25	90
13	35	2:1	0.5	90
14	65	2:1	0.5	90
15	35	4:1	0.5	90
16	65	4:1	0.5	90

The lower arm outlet of the condenser was also directed to the sink for the removal of water formed during the reaction. The removal of the water equally enhances the formation of ethyl ethanoate. The reaction was carried out for 30 *minutes* and stopped. The yield of ethyl ethanoate in the beaker was measured and recorded. Similarly, the procedure was repeated for other experimental runs (2 to 16) while considering the temperature, mole ratio of bioethanol to ethanoic acid, catalyst concentration and the reaction time as illustrated in Table 1 of the experimental matrix for the 2^4 factorial design.

RESULTS AND DISCUSSION

Herein, the 2^4 factorial design enabled the optimization of the influence of the temperature, the mole ratio of bioethanol to ethanoic acid, catalyst concentration and esterification time on the yield of ethyl ethanoate. The analysis of variance (ANOVA) for the parameters interactions are discussed while the characterizations of the kinematic viscosity, specific gravity, flash point, refractive index, distillation and Fourier transform infrared (FTIR) are presented.

3.1 Optimization of Esterification Process

The esterification process is the reaction of alcohol and carboxylic acid for the production of ester. The produced bioethanol was reacted with ethanoic acid via an esterification reaction to enhance conversion to ethyl ethanoate. The production of ethyl ethanoate was optimized by investigating the effects of process variables on the yield of the product using a 2^4 factorial design.

The process variables considered for the esterification process are reaction temperature, the mole ratio of bioethanol to ethanoic acid, catalyst concentration and time of esterification respectively.

Table-2 Ethyl Ethanoate Yield at Varying Esterification Process Conditions

Run	Temperature (°C)	Mole Ratio (g/mol)	Catalyst Concentration (%)	Time (minutes)	*Yield* (%)
1	35	2:1	0.25	30	25
2	65	2:1	0.25	30	46
3	35	4:1	0.25	30	18
4	65	4:1	0.25	30	35
5	35	2:1	0.5	30	20
6	65	2:1	0.5	30	40
7	35	4:1	0.5	30	16
8	65	4:1	0.5	30	30
9	35	2:1	0.25	90	84
10	65	2:1	0.25	90	98
11	35	4:1	0.25	90	78
12	65	4:1	0.25	90	94
13	35	2:1	0.5	90	80
14	65	2:1	0.5	90	96
15	35	4:1	0.5	90	75
16	65	4:1	0.5	90	93

Each of these process parameters was studied at two specified levels of high and low values respectively and the summary of the results obtained was presented in Table 2. According to Table 2, the optimum yield of ethyl ethanoate was obtained at the optimal experimental conditions of a temperature of 65℃, the mole ratio of bioethanol to ethanoic acid of 2:1, catalyst concentration of 0.25 *wt* % and esterification time of 90 *minutes* respectively. This value was better than the 80 % conversion reported by Nada *et al*. (2010). The low yield of ethyl ethanoate reported by Nada *et al*. (2010) could be attributed to the fact that the researcher considered only the process parameters of temperature, the mole ratio of ethanol to acetic acid and time respectively and the variations of the parameters affects the yield of the product. The better yield of ethyl ethanoate obtained in this investigation can also be linked to the catalyst used in the experiment which drives the conversion to the right in favour of the product formation and differences in the chemical composition of the bioethanol used which is confirmed by the values obtained from the characterization of the produced bioethanol as presented in Table 2. A detailed analysis of the effects of the different esterification process parameters on the yield of ethyl ethanoate was carried out as below.

Nada *et al*. (2010) reported that the rate of esterification and the yield of ethyl ethanoate are positively affected by temperature and varied the esterification temperature from 50 ℃ to 60 ℃. Although it was reported by Nada *et al*. (2010), that 60 ℃ is the optimal temperature for the production of ethyl ethanoate, various temperatures will give different degrees of conversion concerning the catalyst utilized. The effect of temperature on the yield of ethyl ethanoate was investigated in this study by varying the temperature at 35 ℃ for low level and 65 ℃ for high-temperature level as was shown in Fig. 1.

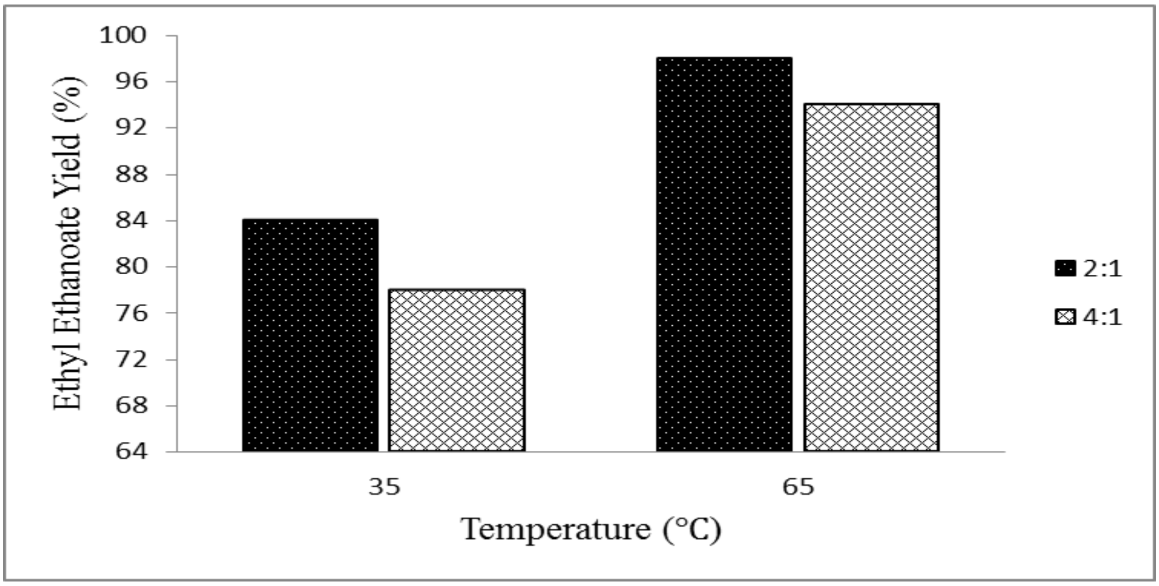

Fig. 1 Effect of Temperature on the Yield of Ethyl Ethanoate

The high-temperature level of 65 ℃ was chosen to avoid the loss of bioethanol to evaporation considering the reactant's boiling point. As shown in Fig. 1, experiments performed at 65 ℃ gave the optimum yield of ethyl ethanoate and the effects of temperature on the process can be linked to its effect on substrate solubility as well as its direct influences on the reaction (Facioli and Barrera-Arellano, 2001). It was found that increasing the temperature of the esterification process, increases the rate of conversion to ethyl ester. The yield of ethyl ethanoate at the temperature of 35 ℃ was 84% with the process conditions of mole ratio of bioethanol to ethanoic acid, catalyst concentration and reaction time kept constant at 2: 1, 0.25 wt% and 90 minutes respectively but increased to 98% as the temperature of esterification was increased up to 65 ℃ under the same reaction process conditions. The process conditions of mole ratio of bioethanol to ethanoic acid of 4: 1, catalyst concentration 0.25 wt% and reaction time of 90 minutes gave the yield of 78% at the low-level esterification temperature of 35 ℃ and 94% ethyl ethanoate yield at the high-temperature level of 65 ℃ under the same reaction process conditions. This finding agrees with the work of Vieira *et al*. (2006), Radzi *et al*. (2011) and Nada *et al*. (2010) who reported an increasing effect of temperature on the product conversion.

Nada *et al.* (2010) and Radzi *et al.* (2011) reported that the mole ratio of bioethanol to ethanoic acid is an important esterification process parameter affecting the optimal yield of ethyl ethanoate. It was ensured in this work that the mole ratio of bioethanol to ethanoic acid was varied at 4:1 for high level and 2:1 for low level. It is important to mention that a high molar excess of bioethanol to ethanoic acid of 2:1 and 4:1 was used to ensure that the excess bioethanol concentration enhances the drive for the product conversion by the limited ethanoic acid. Hence, ethanoic acid was used in a limited capacity to facilitate the yield of ethyl ethanoate. The result of this work shows that the optimum yield of ethyl ethanoate was obtained at the lowest studied molar ratio of bioethanol to ethanoic acid as illustrated in Fig. 2. The process conditions of temperature, catalyst concentration and reaction time of 35 ℃, 0.25 wt% and 90 minutes gave the yield of 84% at the low-level esterification mole ratio of bioethanol to ethanoic acid of 2:1 and 78% ethyl ethanoate yield at the high mole ratio of bioethanol to ethanoic acid of 4: 1under the same reaction process conditions. The optimal ethyl ethanoate yield of 98% was obtained using the mole ratio of bioethanol to ethanoic acid of 2:1 at the temperature of 65 ℃, catalyst concentration of 0.25 wt% and esterification time of 90 minutes compared to 94% of ethyl ethanoate yield obtained under the same experimental conditions while using excess mole ratio of bioethanol to ethanoic acid of 4:1. This pattern of result on the yield of ethyl ethanoate at bioethanol to ethanoic acid mole ratio could also be traced to the fact that esterification reaction was catalyzed with acid and could also be attributed to the fact that the limiting reactant defines the yield of ethyl ethanoate.

The effect of this factor in this work agrees with the findings of Nada *et al.* (2010), Abiney *et al.* (2008), Calver *et al.* (2007), Vieira *et al.* (2006) and Kirbaslar *et al.* (2001) who reported a high yield of ethyl ester using a low level of bioethanol to ethanoic acid mole ratio.

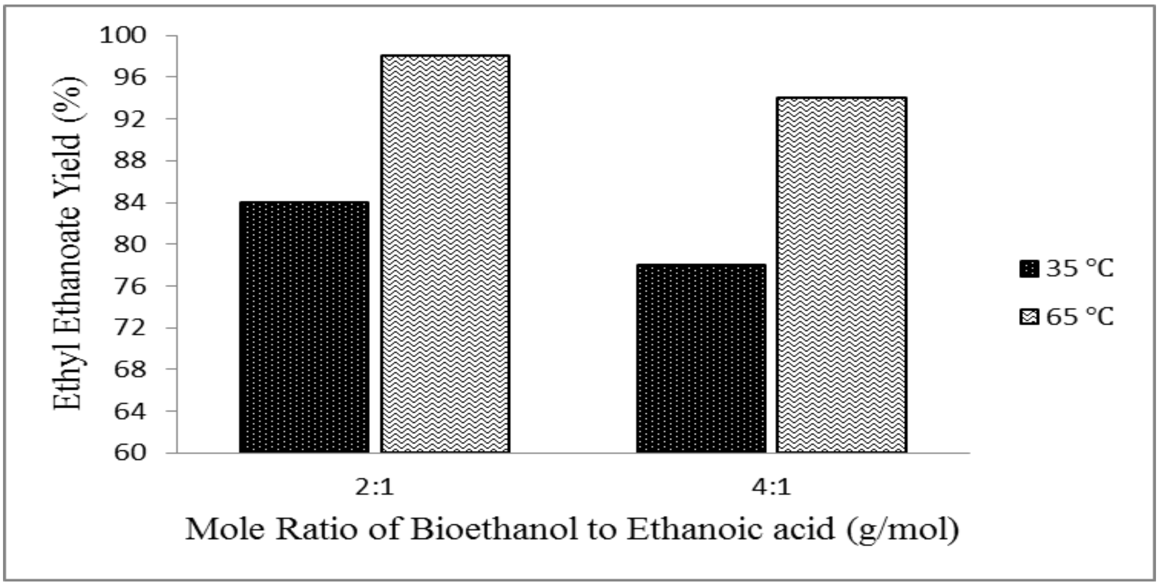

Fig. 2 Effect of Mole Ratio on the Yield of Ethyl Ethanoate

Also investigated in this work and shown in Fig. 3, is the effect of catalyst concentration on the yield of ethyl ethanoate. Catalyst concentration was varied in this study at 0.25 wt % and 0.5 wt% for the low and high levels of reaction respectively. The yields of ethyl ethanoate using the low and high levels of catalyst concentration for the experiment are shown in Fig. 3. Catalyst concentration has little effect on the per cent yield of ethyl ethanoate under the same experimental conditions as was observed in Fig. 3.

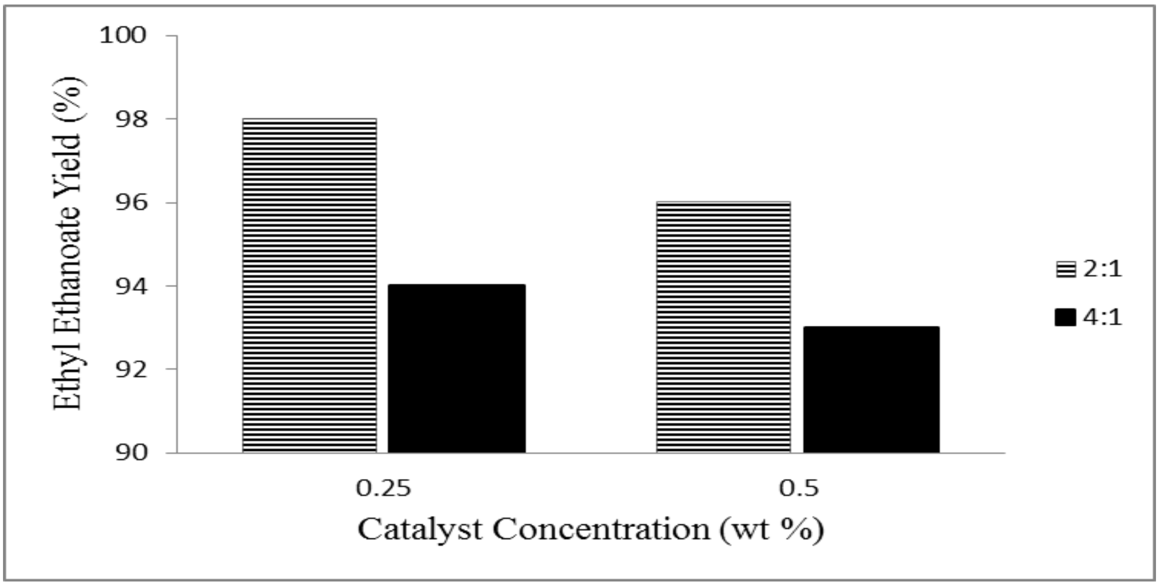

Fig. 3 Effect of Catalyst Concentration on the Yield of Ethyl Ethanoate

The experimental conditions of the temperature of 65 °C, the mole ratio of bioethanol to ethanoic acid of 2: 1 and esterification time of 90 minutes produced the optimum ethyl ethanoate yield of 98% using 0.25 wt% of sulphuric acid and 96% of ethyl ethanoate yield with 0.5 wt%.

The yield of ethyl ethanoate at the catalyst concentration of 0.25 wt% was 94% with the process conditions of temperature, the mole ratio of bioethanol to ethanoic acid and reaction time kept constant at 65 ℃, 4:1 and 90 minutes respectively but decreased to 93% as the catalyst concentration was increased up to 0.5 wt% under the same reaction process conditions. This pattern of result is because catalyst does not take part in the reaction but only drives the reaction in favour of ethyl ethanoate production. Time of esterification is an important process parameter affecting the yield of ethyl ethanoate. Esterification process reaction time was varied in this work for low and high levels of the 2^4 experimental design factorial at 30 minutes and 90 minutes respectively as presented in Fig. 4. It was observed that the esterification process reaction time has a tremendous effect on the per cent yield of ethyl ethanoate. Generally, the relative percentage conversion of ethyl ethanoate was increased with increasing reaction time.

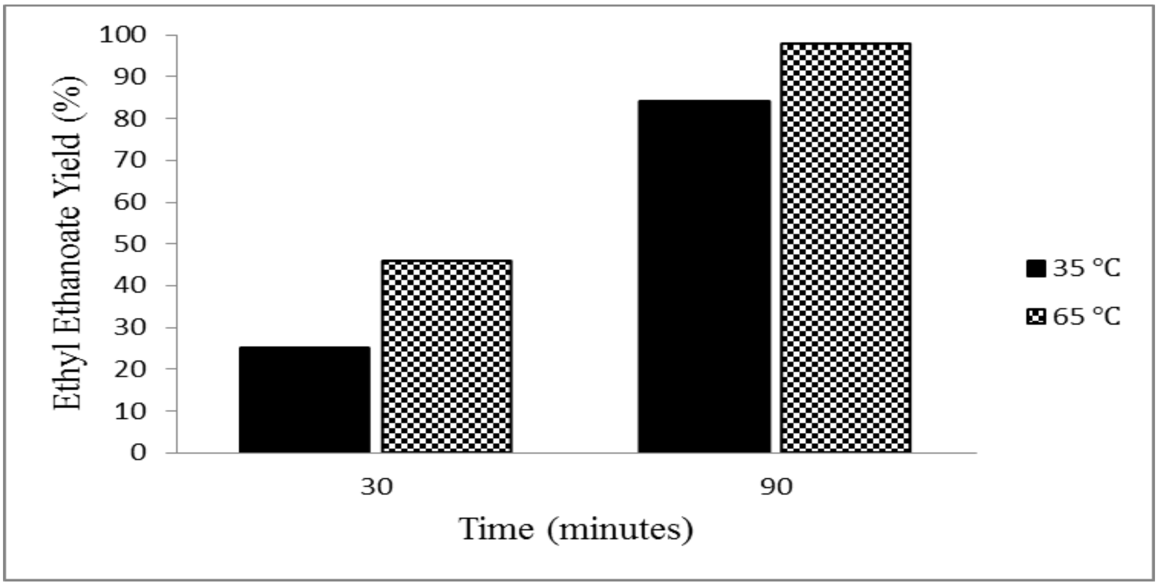

Fig. 4 Effect of Esterification Time on the Yield of Ethyl Ethanoate

The optimum yield of ethyl ethanoate under the experimental conditions of the temperatures of 35 ℃ and 65 ℃, the mole ratio of bioethanol to ethanoic acid of 2: 1 and catalyst concentration of 0.25 wt% was obtained as 25% and 46% for the low levels of esterification time of 30 minutes and 98% and 94% for the high levels of esterification time of 90 minutes respectively. The differences in the ethyl ethanoate yield observed at the same experimental conditions shows the tremendous effect of time of esterification on the product yield and the result corresponds with the work of Radzi *et al*. (2011).
The analysis of variance was carried out using design expert software on the 2^4 esterification results of ethyl ethanoate yield presented in Table 2. The results of the effects of the four process variables of Temperature (A), Mole ratio (B), Catalyst concentration (C) and Time of the reaction (D) presented in Table 3 were obtained via the design expert software. Esterification time of reaction and temperature had the highest positive effect of 58.50 and 17 respectively while the mole ratio of bioethanol to ethanoic acid and catalyst concentration had negative effects of – 6.25 and – 3.5 respectively on the esterification process. Similarly, the interactions of the process variables were analysed. Hence, BD, ABD, CD, ACD, BC and ABCD have the highest effects of 1.75, 1.75, 1, 1, 0.75 and 0.25 respectively among the process variables interactions. The interactions of AB, AC, AD, ABC and BCD has the negative and nil effects of – 0.75, 0, −1, −0.25 and −0.25 respectively.

Table-3 Factorial Effects on Esterification Process using 2^4 Design Technique

Intercept Factor	Effects	Sum of Square	% Contribution
A= *Temperature*	17	2312	7.65742
B= *Mole Ratio*	-6.25	312.5	1.03501
C= *Catalyst Conc.*	-3.5	98	0.324579
D= *Time*	58.5	27378	90.6768
AB	-0.75	4.5	0.0149041
AC	0	0	0
AD	-1	8	0.0264963
BC	0.75	4.5	0.0149041
BD	1.75	24.5	0.0811448
CD	1	8	0.0264963
ABC	-0.25	0.5	0.00165602
ABD	1.75	24.5	0.0811448
ACD	1	8	0.0264963
BCD	-0.25	0.5	0.00165602
ABCD	0.25	0.5	0.00165602
Lack of fit Residual	-	0	0
Pure Residual	-	8.9514	0.0296473

However, Table 3 shows that esterification reaction time has the highest percentage contribution of 90.6768 % on the ethyl ethanoate yield, followed by the temperature of esterification with 7.65742 %, mole ratio of bioethanol to ethanoic acid of 1.0350 % and catalyst concentration of 0.324579 %. The percentage contributions of the process variables interactions were observed to be very negligible on the yield of the ethyl ethanoate. The Model F-value of 3596.79 implies that the model is significant. There is only a 0.01% chance that a model F-Value of this large could occur due to noise. Values of the P-Value Prob > F less than 0.0500 indicate that the model terms are significant. In this case A, B, C, D, AB, AD, BC, BD, CD, ABD, ACD with 0.0001, 0.0001, 0.0001, 0.0001, 0.0119, 0.0016, 0.0119, 0.0001, 0.0016, 0.0001, 0.0016 are significant model terms. Values greater than 0.1000 indicate that the model terms are not significant. Therefore, AC, ABC, ACD and ABCD have insignificant model terms of 1.0000, 0.3585, 0.3585 and 0.3585 respectively. The R-squared analysis result presented in Table 4 shows that the Predicted R-Squared of 0.9988 is in reasonable agreement with the Adjusted R-Squared of 0.9994, thus validating the authenticity of the model. Adequate Precision measures the signal of the model to noise ratio. A ratio greater than 4 is desirable. The ratio of 155.040 obtained in this model indicates an adequate signal and shows the correctness of the model to navigate the design space.

Table-4 R-Squared Values of Bioethanol Esterification Factorial Design

Term	Value
R-Squared	0.9997
Adjusted R-Squared	0.9994
Predicted R-Squared	0.9988
Adequate Precision	155.040
Standard Deviation	0.75
Mean	58.00
C. V%	1.29

The process parameters and interactions of A, D, BC, BD, CD, ABD, ACD and ABCD has a positive coefficient estimates of 8.50, 29.25, 0.37, 0.87, 0.50, 0.88, 0.50 and 0.12 respectively.

The positive coefficient estimate depicts that the process variables cum their interactions has a direct proportionality to the yield of ethyl ethanoate while B, C, AB, AD, ABC and BCD with the negative coefficient estimate of -3.13, -1.75, -0.38, -0.50, -0.12 and -0.12 shows an inverse proportionality relative to the yield of ethyl ethanoate. The coefficient estimates are presented in Table 5.

Table-5 Summary of Analysis of Variance (ANOVA) of the 2^4 Design Factorial

Source	Sum of Squares	Degree of Freedom	Mean Square	F -value	Coefficient Estimate	P-value Prob>F
Model	30184.00	15	2012.27	3596.79	58.00	<0.0001
A	2312.00	1	2312.00	4132.54	8.50	<0.0001
B	312.50	1	312.50	558.57	-3.13	<0.0001
C	98.00	1	98.00	175.17	-1.75	<0.0001
D	27378.00	1	27376.00	48936.26	29.25	<0.0001
AB	4.50	1	4.50	8.04	-0.38	0.0119
AC	0.00	1	0.00	0.00	0.00	1.0000
AD	8.00	1	8.0	14.30	-0.50	0.0016
BC	4.50	1	4.50	8.04	0.37	0.0119
BD	24.50	1	24.50	43.79	0.87	<0.0001
CD	8.00	1	8.00	14.30	0.50	0.0016
ABC	0.50	1	0.50	0.89	-0.12	0.3585
ABD	24.50	1	24.50	43.79	0.88	<0.0001
ACD	8.00	1	8.00	14.30	0.50	0.0016
BCD	0.50	1	0.50	0.89	-0.12	0.3585
ABCD	0.50	1	0.50	0.89	0.12	0.3585
Residual	8.9514	16	0.56			
Total	30192.95	31				

Hence, the linear regression model designed for the relationship among the process variables of temperature, the mole ratio of bioethanol to ethanoic acid, catalyst concentration and esterification time on the yield of ethyl ethanoate was developed as shown in Equation 1.

$$Yield = 58.00 + 8.50\,A - 3.13\,B - 1.75\,C + 29.25\,D - 0.38\,AB + 0.00\,AC - 0.50\,AD + 0.37\,BC + 0.87\,BD + 0.50\,CD - 0.12\,ABC + 0.88\,ABD + 0.50\,ACD - 0.12\,BCD + 0.12\,ABCD \quad (1)$$

The developed model equation which illustrates the relationship among the process variables of the esterification process and the yield of ethyl ethanoate was simulated with design expert software.

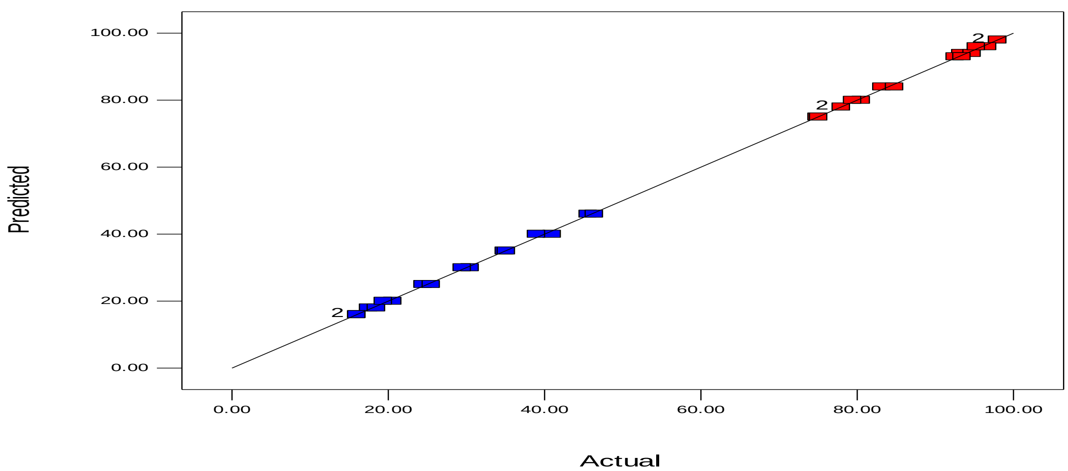

Fig. 5 Plot of Predicted Yield against the Actual Yield of Ethyl Ethanoate

Ethyl ethanoate yield was predicted within the range of the experimental values using design expert software. The predicted yield of ethyl ethanoate was plotted against the experimental yield of ethyl ethanoate and shown in Fig. 5. A straight line without a lack of fit was obtained which shows the correctness of the agreement between the experimental values and the model equation.

3.2 Characterization of the Ethyl Ethanoate

The produced ethyl ethanoate from bioethanol and ethanoic acid in the presence of sulphuric acid catalyst was characterized to ascertain the suitability of the ethyl ethanoate as a solvent for industrial and laboratory purposes. The results obtained from the various analyses carried out on ethyl ethanoate are presented in Table 6. Kinematic viscosity is the resistance to the flow of a liquid substance under gravity and is loosely referred to as the thickness of a liquid. The efficiency of ethyl ethanoate as an aprotic solvent is dependent on the kinematic viscosity of the compound. The viscosity of ethyl ethanoate was obtained in this study and presented in Table 6 as $0.5 \text{ x } 10^3$ cst, 0.02×10^3cst, and $0.004 \text{ x } 10^3$ cst at the temperatures of 20 ℃, 40 ℃ and 60 ℃ respectively. This value falls within the ASTM standard for the kinematic viscosity of ethyl ethanoate. However, the values of the viscosity of the produced ethyl ethanoate obtained in this work show that it can efficiently function as an industrial solvent. The kinematic viscosity of ethyl ethanoate reported in this work shows appreciable correspondence with the kinematic viscosity of 0.549 *cst* reported by Chevalier (1995) at 20 ℃. The specific gravity of ethyl ethanoate is known loosely as the relative heaviness of the solvent. Results presented in Table 6 signify that the specific gravity of the produced ethyl ethanoate was obtained as 0.854 kg/L and 0.896 kg/L at the observed temperature of 26 ℃ and standard temperature 15 ℃ respectively. This result falls within the standard of ASTM and appreciably agrees with the work of Deosarkar (2012) who reported the specific gravity of ethyl ethanoate to be 0.8906 kg/L at 15 ℃. The result of the flashpoint analysis of ethyl ethanoate was also presented in Table 6 and the value of 7.0 ℃ obtained falls within the ASTM standard for protic solvent. Flashpoint is the lowest temperature at which ethyl ethanoate ignites on the application of flame.

Table-6 Properties of Ethyl Ethanoate

S/N	Property Test	Units	Experimental Result	ASTM Standard
1	Kinematic Viscosity			
	@ 20 ℃	cst	0.5×10^3	0.1×10^3-0.005×10^3
	@ 40 ℃	cst	0.02×10^3	
	@ 60 ℃	cst	0.004×10^3	
2	Specific Gravity	kg/L		0.850-0.950
	@ 26 ℃	kg/L	0.854	
	@ 15 ℃	kg/L	0.896	
3	Flash Point (Open Cup)	℃	7.0	5.0-15.0
4	Refractive Index	-	1.370	1.370-1.374
5	Distillation			
	IBP			70-80
	5%	℃	68	
	10%	℃	70	
	30%	℃	72	
	50%	℃	72	
	70%	℃	73	
	90%	℃	74	
	100%	℃	75	
	EBP	℃	76	
	Total Recovery = 100	℃	76	
6	Sulphur Content	wt%	0.00026	0.05 max

Flashpoint is an important physical property of liquids that defines their fire hazards and risks of explosion. It is an important property that ensures the safety of industrial products and their applications. The low flash point of ethyl ethanoate signifies its efficiency for use in the industries as a solvent for varied applications and care should be taken because of its flammable and combustible characteristics. A Refractive index is a physical property of a substance that defines its purity relative to the density of the substance. Refractive index decreases with a decrease in density as the temperature of the substance increases. Table 6 shows that the refractive index of the produced ethyl ethanoate is 1.370 this value falls within the standard recommendations of industrial solvents by ASTM. The result of this work is small compared with the ethyl ethanoate refractive index of 1.374 reported by El-Dossoki (2007) which could be a result of the Abbe refractometer used in this study. However, both values are still within the range of ethyl ethanoate refractive index under which the product functions effectively as an industrial solvent. The distillation characteristics investigations on the produced ethyl ethanoate were obtained as presented in Table 6. The initial boiling point (IBP), 5, 10, 30, 50, 70, 90 and 100 % recovery and end of boiling point (EBP) of the ethyl ethanoate were obtained as 68, 70, 72, 72, 73, 74, 75 and 76 ℃ respectively. The total recovery of 100% obtained significantly shows that the produced ethyl ethanoate is free from impurities and thus enhances its efficiency as an aprotic solvent. The boiling range of ethyl ethanoate obtained in this work shows considerable agreement with the standard of ASTM on the recommended boiling range for industrial solvents. The sulphur content of the ethyl ethanoate was also analyzed and presented in Table 6 as 0.00026 and this value was found very negligible compared with 0.05 max sulphur content recommended by ASTM standard. The value of sulphur obtained in this study equally shows that there is an appreciable negligible number of impurities present in the compound. The insignificant presence of sulphur impurities in the solvent is a clear test of the potency and efficacy of bioethanol as an industrial solvent.

The importance of infrared spectroscopic analysis on ethyl ethanoate was for the determination of the chemical functional groups in the product. As infrared radiation was passed through the ethyl ethanoate sample, some of the radiations were absorbed by ethyl ethanoate while some were transmitted. Table 7 shows the spectrum of infrared radiation and intensity produced by the molecular absorption and transmission of ethyl ethanoate.

Table-7 FTIR Peak and Intensity of the Produced Ethyl ethanoate

Peak	Intensity
447.5	18585
1032.92	72.885
1249.91	81.513
1387.83	86.574
1731.17	84.353

An infrared wavelength of 447.5 cm^{-1} with the intensity of 18.585 falls within the alkyl halides absorption region of the $C - X$ (X=F, Cl, Br or I) functional group which absorbs at 800-400 cm^{-1}. The second peak with the vibration frequency of 1032.92 cm^{-1} and the intensity of 72.885 shows the presence of $C - O$ and $C - O - C$ stretch bond of alcohols and dialkyl ethers which absorbs at the vibration frequency range of 1260-1000cm^{-1} and 1300-1000 cm^{-1} respectively. It is evident from the third spectrum with an infrared vibration of 1249.91 cm^{-1} and the intensity of 81.513, that there is the presence of $C - C(O) - C$ or $C - O$ aliphatic stretch bond of esters functional group which absorbs at the frequency region of 1260-1230 cm^{-1} for acetates. This functional group confirms the presence of ethyl ethanoate which is also called ethyl acetate. An infrared spectrum of 1387.83 cm^{-1} and intensity of 86.574 from the fourth peak shows that the $C - H$ plane bend of the alkane functional group absorbs at the wavelength region of 1430-1290 cm^{-1}. The fifth peak with a wavenumber of 1731.17 cm^{-1} and intensity of 84.353 indicates that there is the presence of molecular motion of $C = O$ strong stretch of carboxylic acids which absorbs at the molecular motion frequency range of 1730-1700 cm^{-1}. The molecular motion of 1731.17 cm^{-1} also shows proximity with the absorption range of 1760-1670 cm^{-1} for aldehydes, ketones, carboxylic acids and esters. However, the functional groups of the aldehydes, ketones, carboxylic acids and esters have $C = O$ molecular vibration.

The spectrum of 2952.15 cm^{-1} with an intensity of 82.053 represents the sixth peak. The spectrum defines the presence of $C - H$ with a strong stretch of alkane bond which absorbs at the frequency range of 2960 to 2850 cm^{-1}. This functional group confirms the presence of a linear aliphatic chain. The molecular vibration of 3365.9 $cm^{-1}$and the intensity of 74.866 was exhibited by the seventh peak of the infrared spectrum. The spectrum shows the presence of the $O - H$ broad absorption band which occur at the frequency range of 3600-3200 cm^{-1}. The findings of this work show agreement with the work of Sherman (1996), Coates (2000) and Stuart (2002). It was however established that the produced ethyl ethanoate consists of $C - O$, $C - O - C$, $C - C(O) - C$ $C - H$, $C = O$ and $O - H$ functional groups. The functional groups present in the compound have however identified the product as ethyl ethanoate.

CONTRIBUTION TO KNOWLEDGE

In this study, ethyl ethanoate was successfully produced from a cellulosic bioethanol using an organic acid. In addition, the optimum conditions for the temperature, the mole ratio of bioethanol to ethanoic acid, catalyst concentration and esterification time of 65 ^{o}C, 2:1, 0.25 wt% and 90 minutes, respectively were obtained using 2^4 factorial design optimization technique. The developed model equation in this study enables fast production of ethyl ethanoate using the defined values and the properties of ethyl ethanoate corroborated effectively with the standard.

CONCLUSION

It was concluded that temperature, the mole ratio of bioethanol to ethanoic acid, catalyst concentration and time of esterification are the most significant parameters affecting ethyl ethanoate yield via the optimum yield of 98% obtained by 2^4 factorial design at the optimum experimental conditions of a temperature of 65 °C, the mole ratio of bioethanol to ethanoic acid of 2: 1, catalyst concentration of 0.25 wt % and esterification time of 90 minutes. The produced ethyl ethanoate shows the potency of a good protic solvent through the results of the kinematic viscosity of 0.5 x10^3 cst, 0.02 x10^3cst and 0.004 x10^3 cst, the specific gravity of 0.896 kg/L, the flashpoint of 7.0 °C, the refractive index of 1.370, distillation boiling range of 68 °C to 76 °C and sulphur content of 0.00026 wt% conforming to ASTM standard specifications on laboratory and industrial solvents. It can be concluded from the analysis of variance that esterification time has the highest effect and percentage contributions of 58.50 and 90.6768 respectively followed by temperature with the effect and percentage contribution of 17 and 7.65742. Mole ratio of bioethanol to ethanoic acid and catalyst concentration had a negative effect of -6.25 and -3.5 with the percentage contributions of 1.03501 and 0.324579 respectively. The R-squared of 0.9997 with the Predicted R-Squared of 0.9988 shows agreement with the Adjusted R-Squared of 0.9994 and validates the authenticity of the model and the interactions of the process parameters. A simple polynomial regression model that can predict the yield of ethyl ethanoate has been developed and represented as Yield = 58.00 + 8.50A - 3.13B - 1.75C + 29.25D - 0.38AB + 0.00AC - 0.50AD + 0.37BC + 0.87BD + 0.50CD - 0.12ABC + 0.88ABD + 0.50ACD - 0.12BCD + 0.12ABCD.

CONFLICTING INTERESTS DECLARATION

The author declared no potential conflicts of interest.

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