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Optimisation of acid hydrolysis in ethanol production from prosopis juliflora

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Abstract: Lignocellulosic materials (eg.Prosopis juliflora) can be utilized to produce ethanol, a promising alternative energy source for the limited crude oil. This study involved optimization of acid hydrolysis in ethanol production from prosopis juliflora. The conversion of prosopis juliflora to ethanol can be achieved mainly by three process steps: pretreatment of prosopis juliflora wood to remove lignin and hemicellulose, acid hydrolysis of pretreated prosopis juliflora to convert cellulose into reducing sugar (glucose) and fermentation of the sugars to ethanol using Saccharomyces cerevisiae in anaerobic condition. A two level full factorial design with four factors, two levels and two replicas (2^4*2=32 experimental runs) was applied to optimize acid hydrolysis and study the interaction effects of acid hydrolysis factors, namely, acid concentration, solid fraction, temperature, and time. An optimization was carried out to optimize acid hydrolysis process variables so as to determine the best acid concentration, solid fraction, temperature, and contact time that resulted maximum ethanol yield. The screening of significant acid hydrolysis factors were done by using the two-level full factorial design using design expert® 7 software. The statistical analysis showed that the ethanol yield of (40.91% (g/g)) was obtained at optimised acid hydrolysis variables of 0.5%v/v acid concentration, 5%w/w solid fraction, 105.01°C temperature, and 10 minutes hydrolysis time.

Keywords: Prosopis Juliflora, Pretreatment, Hydrolysis, Fermentation, 2 Level Factorial, Optimization

1. Introduction

Oil prices are at all times high and there is growing zest to reduce our dependence on oil. It is finite resource, gas supplies and oil reserves are shrinking, will definitely run out in the future. World energy demand is expected to double by 2050 as it is shown in figure 1.1 below. The demand of energy is currently exponentially exceeding the rate of local supply sources, a look beyond the fossils is crucial for long term economic growth and energy security purpose. The volatile situations in the Middle East, where vast reservoirs are, are also creating uncertainties about the availability of the supply. There is also the greater environmental risks associated with exploitation of crude oil (IEA world energy outlook, 2004).

With the diminishing supply of petroleum oil and the political instability in countries where much of the world's oil reserves are found, the prices of petroleum-based fuels are irreversibly going up. As a result of concerns of sustainability, environmental protection, and national energy security, more and more countries have prioritized the importance of renewable energy sources. Ethanol has once again become attractive in the energy marketplace and, in fact, the demand for ethanol has been increasing in recent years (Lin and Tanaka, 2006; Ford, 2004).

Ethanol as well as other bio-fuels produced from plant biomass is alternative to fossil fuels. Ethanol does not add to a net carbon dioxide atmospheric increase thus there is in theory no contribution to global warming. Combustion of ethanol results in relatively low emissions of volatile organic compounds, carbon monoxide and nitrogen oxides. Ethanol was used as transportation fuel at the beginning of 20th century in the U.S., but it was abandoned for fuels processed from petroleum (oil) after World War II because these were cheaper and had higher energy values (Lin and Tanaka, 2006; Ford, 2004). During the last two decades, technology for ethanol production from non-food-plant sources has been developed to the point at which large-scale production could be a reality in the next few years (Mosier, N., et al., 2005). Moreover, agronomic residues such as corn stover (corn cobs

and stalks), sugar cane waste, wheat or rice straw, forestry and paper mill discards, the paper portion of municipal waste, and mainly dedicated energy crops collectively termed 'biomass' can be converted to fuel ethanol (Divya Paruchuri ,December 2008).

1.1. Statement of the Problem

Ethiopia is currently looking at growing high-yielding crops for the production of bio-fuels as alternatives to traditional fuels (petrol and diesel) to address imminent shortages and reduce impacts of climate change. Owing to such phenomenon, and indeed in view of the recent trends in the escalating price of the traditional petro-fuel, biofuel has been gaining greater attention by the Ethiopian government. But due to the increased cost of food crops, producing ethanol using Prosopis juliflora wood is an alternative feed stock: for one thing, Prosopis juliflora is a fast growing tree species and grows in Ethiopia mainly in arid and semi-arid areas of the Rift Valley. And the other reason is it is a highly invasive exotic tree that is spreading in the pastoralist areas of Ethiopia making vast areas of land unavailable for grazing and it is becoming difficult to remove it.Thirdly, when the plant is cut, new off springs is grown from the root in a short period (Hailu Shiferaw et al., 2004). Invasion of rangelands by Prosopis juliflora also caused shortage of grazing land for livestock, which resulted in drastic reduction of livestock number as well as product; thorns damage eyes and hooves of camels, donkeys, and cattle then by poisoning eventually lead to death. Prosopis juliflora is invading potential croplands forcing local farmers with less capital and machinery to abandon their farmland and settlement. In general, this is a matter of serious concern for the life of the local people as pastoralists depending on livestock for their livelihood (Senayit et al., 2004). Due to the above reasons and as Prosopis juliflora is widely available in Ethiopia; we can use Prosopis juliflora as Ethanol feed stock.

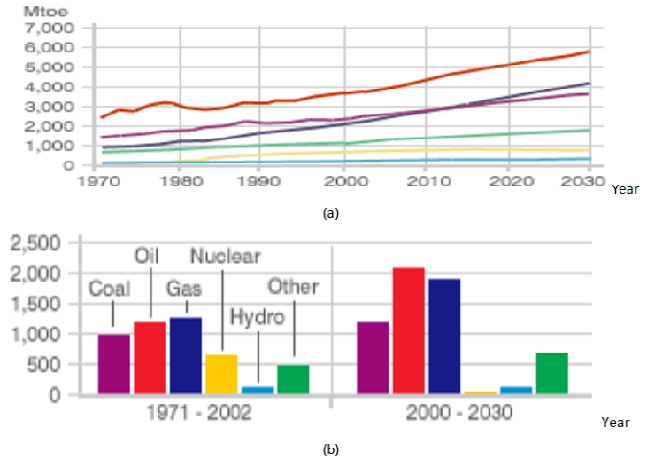


Fig. 1.1. *Illustration of Projected World Energy Demand (a) projected world energy demand and (b) Increase in world primary energy demand by fuel (IEA world energy outlook, 2004).*

MTOE= Million Tones oil equivalent. Method of assessing calorific value of different sources of energy in terms of one tone of oil

2. Lignocellulosic Biomass as Ethanol Feedstock

Lignocellulosic biomass refers to plant biomass that is composed of cellulose, hemicellulose, and lignin. The carbohydrate polymers (cellulose and hemicelluloses) are tightly bound to the lignin. Lignocellulosic biomass can be grouped into four main categories: agricultural residues (including corn stover and sugarcane bagasse), dedicated energy crops, wood residues (including sawmill and paper mill discards), and municipal paper waste(Wikipedia, the free encyclopedia).

2.1. Composition of Lignocellulosic Materials

Cellulose: is a linear polymer of D-glucose units linked by β-1, 4-linked glucose. Cellulose molecules are completely linear and have a strong tendency to form intra and intermolecular hydrogen bond.

Hemicellulose: Hemicelluloses are heterogeneous polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acid (Saha et al., 1997).

Lignin: is a long-chain, heterogeneous polymer composed largely of phenyl propane units most commonly linked by ether bonds (Saha et al., 1997).

Extractives: are woody compounds that are soluble in neutral organic solvents or water. The extractives usually represent a minor fraction (between 1-5%) of lignocellulosic materials. They contain a large number of both lipophilic and hydrophilic constituents. The extractives can be classified in four groups: (a) terpenoids and steroids, (b) fats and waxes, (c) phenolics constituents and, (d) inorganic components (Taherzadeh, 1999).

2.2. Production Methods of Cellulosic Ethanol

There are two primary routes for the production of cellulosic ethanol - biochemical and thermochemical routes. The biochemical route relies primarily on the use of enzymes and other microorganisms and the thermochemical route relies on the application of heat and chemical synthesis. The below process flow diagram (fig. 2.1) shows the basic steps in production of ethanol from cellulosic biomass (Zhu JY et al, 2009).

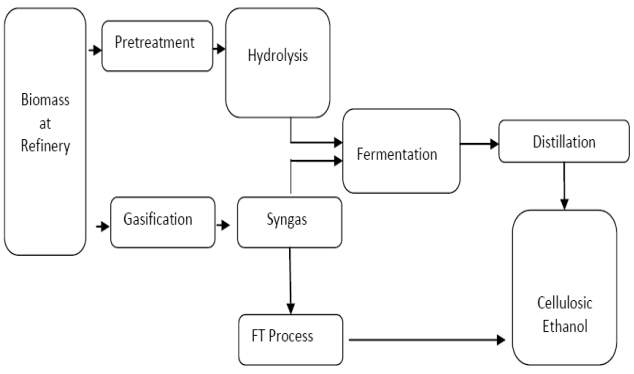


Figure 2.1. *Schematic Diagram of Ethanol productions from lignocellulosic feedstocks (Zhu JY et al., 2009).*

2.2.1. Biochemical Conversion (Sugar Platform)

The biochemical conversion process is similar to the process currently used to produce ethanol from corn starch. Enzymes or acids are used to break down a plant's cellulose into sugars, which are then fermented into liquid fuel. Four key steps are involved. First, feedstock is pretreated by changing its chemical makeup to separate the cellulose and hemicellulose from the lignin in order to maximize the amount of available sugar. Second, hydrolysis uses enzymes or acids to break down the complex chains of sugar molecules into simple sugars for fermentation. Third, fermentation is used to convert the sugar into liquid fuel. Fourth, the liquid fuel is distilled to achieve a 95% pure form (fig. 2.7) (Zhu JY et al., 2009).

3. Materials and Methods

3.1. Materials

The materials used to run all experiments are listed below:

Chemicals: Phenol,Sodium Hydroxide (NaOH, min. assay 98% BDH Chemicals Ltd Poole England cellulose),Sulphuric Acid (H_2SO_4, (98%, England)), Dextrose sugar, Yeast extract, Urea, $MgSO_4.7\ H_2O$, yeast (Saccharomyces cerevisiae) (manufactured in France by S.I. Lesaffre with the strain 'saf-instant').

Equipments: Pycnometer, pH-Meter ,Shaking incubator, Vertical Autoclave, Cutting mill, Autoclavable bio Reactor, Shaker, Ovens- Loading model 100 -800, Beschikung, Funnel, Sieves (mesh size of 2.0 mm, Sortmks-3332, PFEUFFR, Germany), Digital balances (model = Sartorius with 0.01 mg sensitivity, and model EP214C), Vacuum Filter (model = BN 3 STAATLICH, Berlin),Rotary Evaporator (model = D79219, Staufen, Germany).

3.2. Methods

3.2.1. Sample Preparation

Sample preparation process include: manual size reduction (Knife cutting), drying, grinding and sieving. Grinding of Prosopis juliflora into powder form gives the surface area of the sample increased which enhance the contact between hemicellulose and cellulose with dilute acid to reduce cellulose crystallinity.

3.2.2. Pretreatment of Prosopis Juliflora

Acid pretreatment involves the use of concentrated and diluted acids to break the rigid structure of the lignocellulosic material. The most commonly used acid is dilute sulphuric acid (H_2SO_4), which has been commercially used to pretreat a wide variety of biomass types switch grass , corn stover , spruce (softwood) , and poplar (B. Du et al., 2010). In this study dilute sulfuric acid pretreatment method with 1.2% concentration was used. The powder Prosopis juliflora was pretreated inside autoclave and heated at temperature of 135^oC for 30 minutes. Prosopis juliflora powder was fed as batches and every batch contains 300 g of screened Prosopis juliflora powder with a ratio of 10:1(v/w) water to the sample. In sample pretreatment for all batches acid concentration of 1.2%, temperatures of 135^oC and retention time of 30 minutes were used.

3.2.3. Hydrolysis

The cellulose molecules composed of long chains are broken down to "free" the sugar, before it is fermented for alcohol production. Though hydrolysis is of many types, dilute acid hydrolysis is an easy and productive process. Also the amount of alcohol produced in case of acid hydrolysis is more than that of alkaline hydrolysis. Concentrated acid hydrolysis is not used as it is a hazardous and corrosive process and also acid has to be separated out after hydrolysis for the experiment has to be feasible.

The 2 level full factorial experimental design method using Design expert® 7 software was chosen to optimize acid hydrolysis in ethanol production from Prosopis juliflora and to determine the effect of four operating variables of the acid hydrolysis, including acid concentration, solid fraction, temperature (T), and time, and a level of two, with two replica (2^4 *2 =32 experiment) and one response variables which were yield of ethanol.

Table 3.1. *Maximum and minimum values of variables of acid hydrolysis in ethanol production from Prosopis juliflora*

	Variables	Units	Low level (-)	High level (+)
1	Acid concentration	% v/v	0.5	2.5
2	Solid fraction	% w/w	5	10
3	Temperature	(^oC)	105	125
4	Time	Minutes	10	20

3.2.4. Fermentation

Microorganism: All fermentations were carried out using yeast (Saccharomyces cerevisiae) manufactured in France by S.I. Lesaffre with the strain 'saf-instant') in an anaerobic condition.

Fermentation Medium: One liter of production medium was prepared according to the requirements of Saccharomyces cerevisiae, containing 100 gm dextrose, 2gm dry yeast extract, 10 gm Urea, 1gm $MgSO_4.7\ H_2O$ and 1000 ml make up distilled water.

3.2.5. Distillation

Distillation is the method used to separate two liquids based on their different boiling points. However, to achieve high purification, several distillations are required. In this study separation are made by rotary evaporator at a temperature of 85 ^oC.

4. Results and Discussions

To see how well the cubic polynomial model satisfies the assumptions of the analysis of variance (ANOVA), the plots of residuals and residual versus predicted values were analyzed.

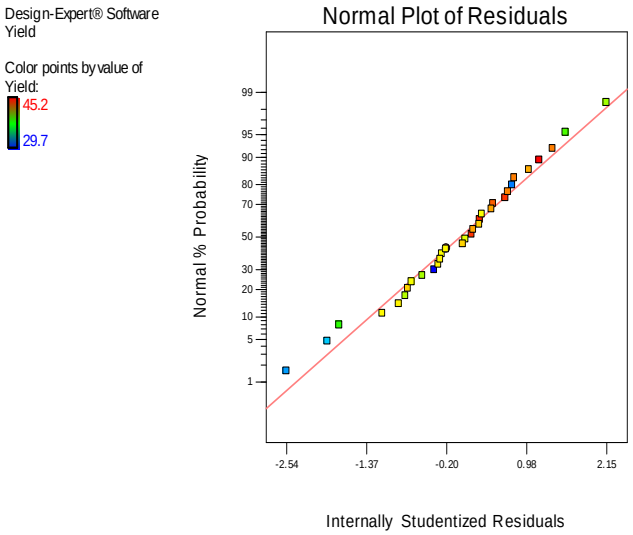


Figure 4.1. *Normal plot of residuals*

The normal probability plot, (Fig. 4.1), indicates the residuals following a normal distribution, in which case the points follow a straight line. This indicates the model satisfies the assumption of ANOVA.

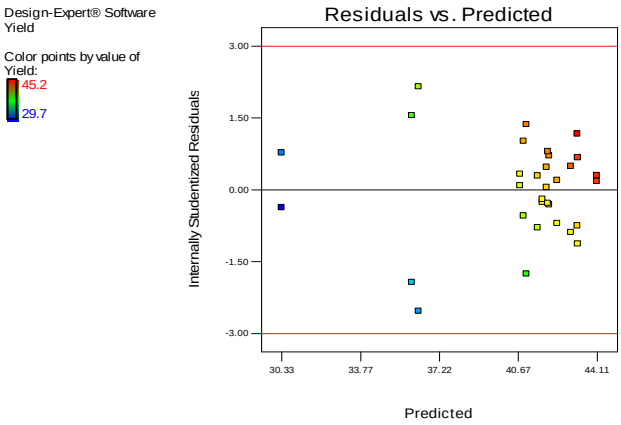


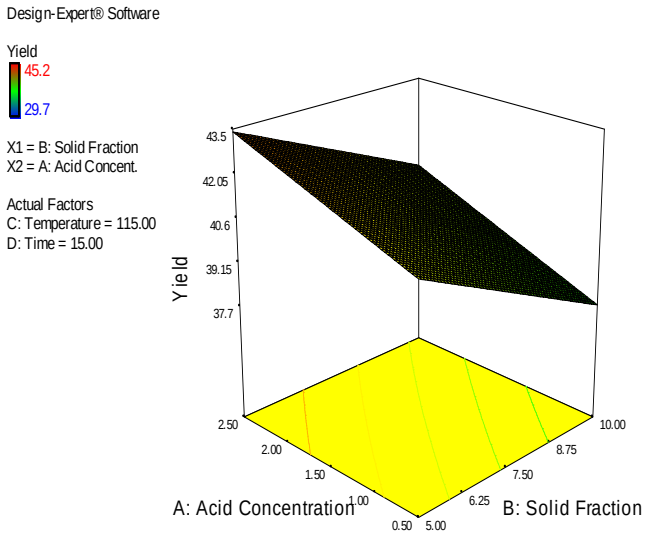
Figure 4.2. *Plot of residuals versus model predicted values*

The plot of the residuals versus the predicted response values (Fig. 4.2), tests the assumption of constant variance. The plot shows constant range of residuals across the graph which is welcome deserving no need for a transformation to minimize personal error.

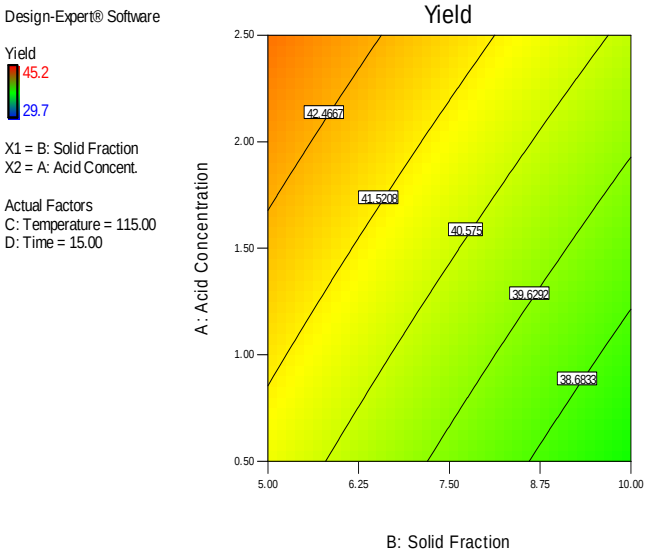
4.1. Interaction Effects

Acid hydrolysis is influenced by different factors and the ethanol yield has a complex relationship with independent variables that contain first, second and third-order polynomials and may have more than one maximum point.

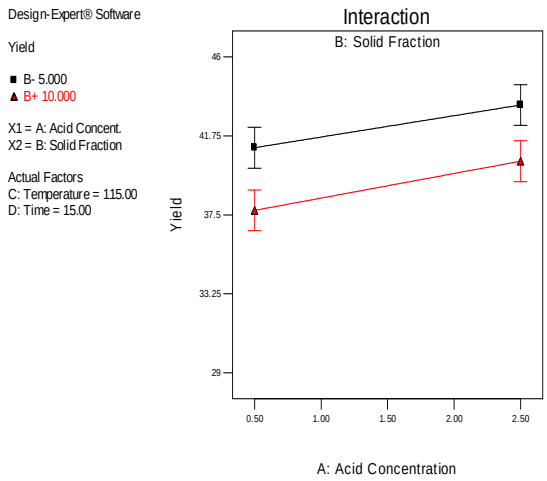
The best way of expressing the effect of any parameter on the yield within the experimental space under investigation was to generate response surface plots of the equation. The three dimensional response surfaces, contours and interactions were plotted in figures (4.3 a, b, c, and d), as a function of the interactions of any two of the factors by holding the other two at average value. In the interaction plots the black line represents low level of variables and the red line represents high level of variables.



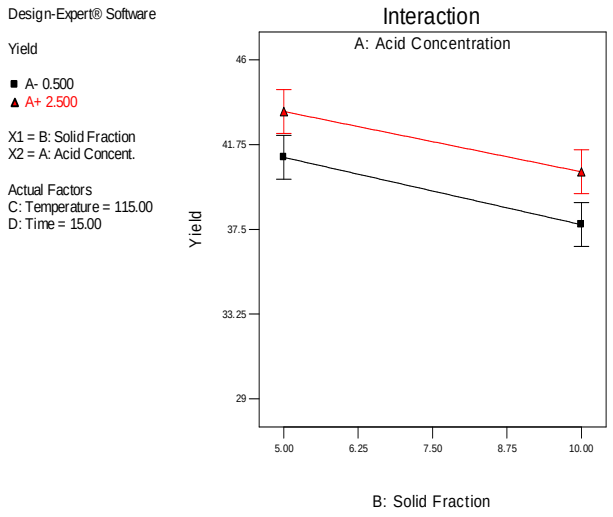
(a)



(b)



(c)



(d)

Figure 4.3. *Response surface plot(a), contour plot (b) and interaction plot (c)and (d) of ethanol yield as a function of acid concentration and solid fraction*

4.2. Optimization

The optimum acid concentration, solid fraction, temperature and time for maximum ethanol yield are 0.50 %v/v, 5.00 %w/w, 105.01^{o}C and 10.00 minutes respectively with 40.9 % ethanol yield.

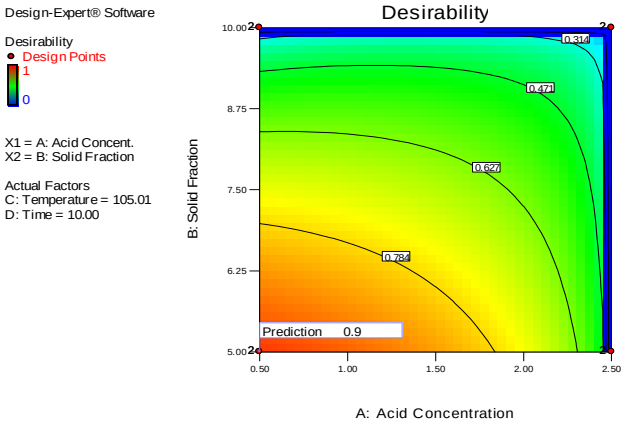


Figure 4.4. *Optimization contours on ethanol yield*

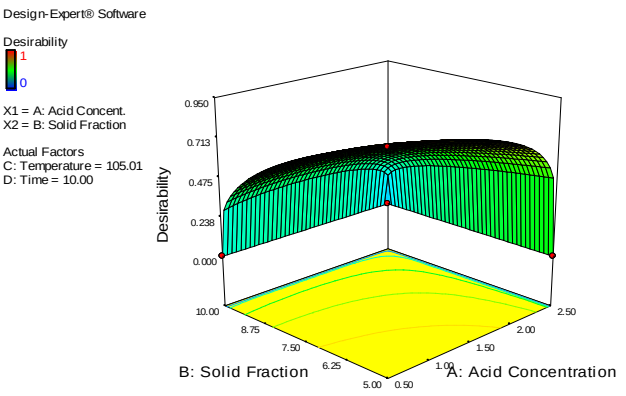


Figure 4.5. *Surfaces of possible optimum solutions*

4.3. Model Validation

As determined by the 2-level factorial design result using Design-Expert® v.7 software, an experiment with acid concentration ,solid fraction, temperature and time was conducted to carry out the effect of the design used. The optimal values test factors were 0.5 % v/v, 5 % w/w, 105.01°C and 10 minutes. The experiment was carried out at the optimized conditions. Ethanol yield of 40.91 (average) obtained and was in good agreement with the predicted one. Therefore the model is considered to be accurate and reliable for predicting the yield of ethanol.

5. Conclusion and Recommendation

5.1. Conclusion

Due to the diminishing of fossil fuel resources, production of ethanol from lignocellulosic material has acquired significance as a fuel for the future. This study examines the possibility of prosopis juliflora wood for ethanol production. The conversion of prosopis juliflora wood to ethanol was carried out with dilute acid pretreatment, dilute acid hydrolysis, fermentation and distillation process steps.

In this study, 2 level full factorial experimental design was used for the optimization of acid hydrolysis process conditions as well as to investigate interaction between acid hydrolysis process factors using Design Expert® 7 software. The effects of acid hydrolysis variables, namely acid concentration, solid fraction, temperature, and time on the ethanol yield were investigated. A cubic polynomial regression model was assumed for predicting response and the probability p- values of 0.0001 indicate the model was highly significance. The choice of the mathematical model was confirmed by variance analysis. It is concluded that the assumed cubic polynomial models satisfactorily explained the effects of the above-mentioned variables on the ethanol yield. Ethanol yield of 40.91% was obtained when optimum conditions were acid concentration 0.5%, solid fraction 5%, temperature of 105.01^{0}C, time of 10 minute, which indicates that at this condition no inhibitors (furfural and HMF) are produced that inhibit the fermentation process steps. Validation experiments verified the availability and the accuracy of the model with desirability 90 %. The predicted value was in agreement with the experimental value (40.91 wt. %). Based on this study, it is evident that the chosen method of optimization was efficient, and reliable.

5.2. Recommendations

Producing ethanol from renewable resources is becoming an important issue for the whole world. Therefore, the work needs to be continued for further development of ethanol production from prosopis juliflora.

It is also, recommend that in this study acid hydrolysis variables are optimised; future studies should include optimisation of pretreatment process, optimisation of fermentation process and optimisation of distillation process

variables to obtain maximum yield of ethanol from prosopis juliflora wood.

Additionally, it is recommend that preliminary design of pilot plant, process development and scale up has to be performed.

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