



Optimization of Two stage concentrated acid hydrolysis Process of biofuel for both sulphuric and hydrochloric acid

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Abstract

The conversion of biomass to soluble sugars for biofuel production has received great interest to be used as an alternative and renewable source of energy. Hemicellulose biomass is potentially applied to contribute to biofuel production to minimize greenhouse gas emissions and global warming. In this work, two stages concentrated acid hydrolysis process was used for the hydrolysis of biomass as a biological resource. Both sulfuric and hydrochloric acids were used and applied by the same concentration (weight by weight) for the hydrolysis process. The effect of acid type on the two stages concentrated acid hydrolysis of biomass has been investigated. The results revealed that hydrochloric acid is more effective than sulfuric acid. In the first stage, the results showed that, increasing the sulfuric acid concentration from (10 to 30 %) (w/w), resulted in enhancing xylose concentration from 6.0 to 9.0 mg/ml compared to 9.0 to 12.0 mg/ml in the case of hydrochloric acid (10 to 30 %). In addition, the second stage results showed that glucose concentration increased from 2.0 to 5.2 mg/ml and xylose was slightly increased from 1.8 to 2.1 mg/ml, using sulfuric acid (20-30%) and total dissolved sugars increased from 4.1 to 8.0 mg/ml. while in the case of hydrochloric acid (20-30%) for the hydrolysis of biomass total dissolved sugars enhanced from 7.3 to 10.0 mg/ml. The results confirmed that both acids are comparable for the biomass hydrolysis process with better enhancements (1.25 – 1.7 times) when applying hydrochloric acid.

Keywords: hydrolysis, biomass, hydrochloric acid, sulfuric acid.

1. INTRODUCTION

Recently, the depletion of fossil fuels and their high prices as well as the concerns of global warming result in looking for alternative strategies for energy production. Biofuels are one of the key alternative choices for the substitution of fossil fuels. Biomass serves as a potential renewable source for the production of gaseous, liquid, and solid biofuels [1]. Millions of tons of residual agriculture waste are harvested and piled every year including sugarcane bagasse, rice straw, wheat straw, and corn stover.

Those wastes must be discharged from the harvested place; the easiest way to remove these solid wastes is burning which pollutes the environment with the toxic gases [2]. Hence, several countries treated these wastes and transferred them to biofuel as the biomass by converting them to soluble sugars

through various techniques. The main components of the biomass are cellulose (40%), hemicellulose (35%), and lignin (25%) [3]. Dissolution of these components is carried out utilizing both acidic and basic hydrolysing agents [4]. In the basic agent's treatment, dissolution is achieved using caustic soda to dissolve lignin giving rise to a soluble content in the biomass comprising a soluble content called black liquor which mainly consist of sodium ligninate. If the resultant sodium ligninate is concentrated enough, it could be used as a complementary industrial fuel (e.g.: paper industry).

Hemicelluloses are also dissolved by the soda addition and high temperature [4]. In case of acidic agent treatment, that is applied to the biomass by sulphuric acid or hydrochloric acid, hemicellulose is firstly hydrolysed to soluble sugars under the high

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Receive Date: 31 December 2021, Revise Date: 21 January 2022, Accept Date: 25 January 2022

DOI: 10.21608/EJCHEM.2022.114020.5187

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temperature, cellulose is degraded as the same conditions and while, lignin conversely precipitated as a solid material as used in the biofuel companies [5].

Hemicellulose which consists mainly of xylose chains, is easily to be hydrolyse more than other component giving soluble xylose sugar with a small amounts of glucose, galactose, and arabinose [6]. Hemicellulose is the weakest component in the group that is firstly hydrolysed at any attack to the biomass whatever the agent is acid, base or hot water (more than 100 °C).

Shekiro et al [7], claimed that the high temperature used is the main factor affecting hemicellulose hydrolysis where the acetyl group is liberated from the biomass under effect of elevated temperature, then linked with CH₃ group forming acetic acid. That process is the cause of the observed pH decrease when hydrolysing hemicellulose with liquid hot water [7].

The increase in the acidity of the dilute acid hydrolysis process is due to the acetyl group liberated from hemicellulose hydrolysis. Cellulose is mainly composed of glucose units connected to each other's with hydrogen bond linked by β1, 4 glycosidic bonds [8]. Cellulose hydrolysis is the challenge of the process where all the ordinary methods such as dilute acid hydrolysis process only hydrolysis about 50% of the total cellulose in the second stage, increasing acid concentration and temperature is found to be useless due to degradation of the glucose units produced to hydroxy methyl furfural (HMF). [8].

Lignin is the component left after biomass hydrolysis where it is precipitated in acidic conditions; the residual lignin precipitated may be used as a fuel to decrease the fuel consumption for the process. [9]. Moreover, this pathway enhances the process economy and decreases its resultant environmental burden.

The main purpose of the biofuel hydrolysis process is to find a cheap and easy way to convert the biomass to soluble sugar, where the processing cost of the operation is a vital agent to be suitable and comparable with the price of the other fuel used such as gasoline. There are many processes currently in use to convert the biomass to a soluble sugar such as Liquid Hot Water (LHW) where the biomass is hydrolysis to a soluble sugar is affected by high temperature more than 200°C. [10]. Even though, many researchers pointed out that the hydrolysis occurs by liberating acetyl group liberated from hemicellulose hydrolysed, (Shekiro et al) [7] claimed that the effect of high temperature is the main factor

for converting the hemicellulose to a soluble sugar after de-acetylating the acetate group by rinsing the biomass in a dilute caustic soda.

The main advantage of the LHW process is proceeding without any chemicals however; it requires high temperature and high pressure. Processing at high temperatures and high pressures implies increased operational costs, harsher working environments, specific and highly-priced construction and fabrication materials, more frequent maintenance and repair of pieces of equipment, and elevated associated risks of pressurized containers.

Regarding the two stage dilute acid hydrolysis process, the first stage includes the reaction of the biomass with dilute acid 0.1-3.0% at temperature range 120 – 130°C for a certain time period where the time is a factor in the nature of the process which is continuous or a batch one. [11]. Sulphuric, hydrochloric or nitric acids are all acceptable and the choice of specific one depends on its price and availability [12-19], The processing time may range from 25 to 35 min. In the batch processing mode and reduced to 5 min in a continuous case processing mode with a high temperature. The yield of the first stage is the hydrolysing of the total hemicellulose to a soluble sugar leaving the cellulose and lignin as a solid material [20].

Cellulose hydrolysis is a complicated process where the dilute acid hydrolysis process can't reach to hydrolyse the total cellulose. Only 50% of the cellulose can be hydrolysed by the second stage dilute acid hydrolyses process [21-24]. The second stage dilute acid hydrolysis process include contacting the biomass lifted from the first stage as a solid which include cellulose and lignin with a dilute acid range from 0.1 – 3.0% at temperature higher more than the first one 140 – 180°C for a certain time period reaching to 30 minutes. For the batch process mode, and 0.1 - 5.0 minutes for the continuous processing mode. [25].

The main advantage of the two stage concentrated acid hydrolysis process is the separation of the main component of the soluble sugars in the biomass, where in the first stage the soluble sugar mainly consists of xylose and the second stage consists mainly of soluble glucose where the two stage concentrated acid hydrolysis process enable for separating the xylose component from the glucose component. Despite the concentrated acid hydrolysis process which; require contacting the biomass with concentrated acid 70% with the biomass [26].

That the total hemicellulose and cellulose hydrolysis occur where the soluble sugar produced

from this process comprising mainly glucose and xylose (soluble sugars) which cannot be separated by the ordinary method [12-19]. However, it requires some extra separation process such as ion exclusion and another separation process which is considered expensive (if it is required to separate the two main components, xylose and glucose).

The main target in biomass hydrolysis is to increase the dissolved sugar yield with the same conditions without any degradation in the sugar to toxic materials such as furfural or HMF. In this work, two stages concentrated acid hydrolysis process was used for the hydrolysis of biomass, both sulphuric and hydrochloric acids were investigated for the hydrolysis process. Applying hydrochloric acid for biomass hydrolysis process found to be more effective than sulphuric acid up to 1.7 times with the same concentration.

2. Experimental

The used raw material obtained from Qena Paper Industries Company in Qena – Egypt that the company produce white paper from chemical bleached bagasse (the solid residual from sugar industry), the bagasse sample de-pithed many times through de-pither and centrifuge, the de-pithed bagasse is washed many times to remove dirty and other odd materials.

Pith is an unfavourable content in the paper industry companies because it is not a fibre and causes several screening problems in paper industries. However, pith is having the same composition of the bagasse exhibiting small difference so it may also potentially use in the biofuel industries. [27]. The de-pithed bagasse sample left for semi closed place switched to air to remove moisture until the moisture of the sample reach the air moisture up to 5 days.

The moisture of the samples was measured manually by taking a known sample weight and dried for 8 hr. in a dryer at 105°C where the moisture is determined by the weight loss before and after the drying of the sample, the moisture results ranged between 6.0 to 6.5% from the total weight., Fig. 1 illustrates the photo of de-pithed bagasse sample.

The amount of Ash was determined by taking a known weight of sample and dried in the furnace at 900°C for 20 minutes, the average value of ash up to 1.2%. Following National Renewable Energy Laboratory (NREL) procedure to determine the percentage of the component in the bagasse that 0.3 gram of the sample reacted with 3 ml of concentrated sulphuric acid 72% (w/w) for about one hour with mixing the slurry every 5.0 minutes and finally

decreasing the concentration of the concentrated acid to 4.0% and boiling the mixture at 121°C for one hour. The cellulose percent is ranged from 37.0 – 39.2%, lignin 24.2-25.6 % and hemicellulose varies from 21.8 – 23%.



Fig. 1: De-pithed bagasse sample from Qena Paper Industrial Company.

All the experiments were carried out at 100 °C, in the concentrated acid hydrolysis process no pressure was required and the start time was recorded at 95°C. Finally, rapid cooling for the samples was required to determine the optimum time.

Soluble sugars determined by High Performance Liquid Chromatography [HPLC] using Shimadzu LC-10 with system controller SCL-10A vp, Pump LC-10 AD vp, equipment refractive index detector RID-10A, Oven CTO-10A vp, Degaser DGU-10A using a Shodex SUGAR SC-LG column. Flow rate 0.7 ml/min, at 80 °C, Injection volume 10 µL, Mobile phase 100% deionized water.

All chemical reagents purchased from alpha chemical laboratory company that used in the paper company laboratory. All chemicals used as received without further purification and all the chemicals prepared by weight by weight and also dry weight loss for all the samples was taken in consideration.

3. Results and Discussion

Several parameters were studied including time, liquid to solid ratio, acid concentration (hydrochloric and sulphuric acid) and temperature. The particle size is kept constant all over the experiments.

3.1 Effect of hydrolysis time

The time required to hydrolysis the biomass maintained not more than 30 minutes for batch process because the sugar yield will be degraded to furfural in the first stage where the xylose is produced and also in the second stage the glucose yield will be degraded to (HMF) [12-19].

Reaction time maintained constant at 30 minutes within all experiments in the first stage to avoid sugar degradation to toxic component such as furfural and (HMF). While, the time of hydrolysis in the second stage fixed in one hour to ensure the complete hydrolysis of cellulose. Whereas, the cellulose is stronger than hemicellulose due to the chains of glucose units connected with B-glycosidic linkage with hydrogen bond which is difficult to be solubilised by the ordinary process. Moreover, through the second stage, the time was maintained constant at one hour to avoid glucose degradation to (HMF) and also to verify the effect of the concentrated acid.

3.2 Effect of liquid to solid ratio

From studying the effect of liquid to solid ratio, it was concluded that, the key factor that controlling the process that as the amount of the liquid added to the system increased, the energy required for heating increased. Moreover, the total volume of the reactor increased. Consequently, as the liquid increased as the sugar yield concentration decreased, therefore every designer wants to decrease the liquid to solid ratio added to the system as possible to reduce the energy consumption, finally to decrease the reactors size and maximize the sugar yield concentration. In accordance, liquid to solid ratio was maintained constant at 10:1.

3.3 Effect of temperature

As the temperature increased the degradation also increased for both hemicellulose and cellulose, meanwhile, as the temperature enhanced the sugar degradation resulted more toxic materials such as furfural and (HMF), so the temperature maintained constant at 100 °C all over the experiments to avoid additional sugar degradation.

3.4 Effect of particle size

The selected particle size used within all the experiments was fixed at 3 cm lengths for both acids, sulphuric and hydrochloric acid, which eliminated any deviation and investigate the effect of the acid only.



Fig. 2: Difference between two types of soluble hydrolysed sugar after biomass hydrolysis process that as the acid concentration increased the total sugar yield increased indicated as brown colour.

3.5 Effect of acid type on the hydrolysis process

3.5.1 First stage concentrated acid hydrolysis

In this stage, about one gram of bagasse with 3.0 mm length reacted with different concentrations of sulphuric acid and hydrochloric acid for 30 minutes with no pressure. The moisture content was 6.5%, liquid to solid ratio 10:1. Also, the most widely used method for monosaccharide detection is High Performance Liquid Chromatography (HPLC).

Monosaccharides such as xylose, glucose, galactose, arabinose which; are soluble in water solutions. [28]. The results showed that, from enhancing concentration of H₂SO₄ from 10% to 30 % xylose concentration increased from 6.0 to 9.0 mg/ml while, on applying hydrolysis by HCl (10 to 30%) the xylose concentration increased from 9.0 to 12.0 mg/ml. Meanwhile, using HCl for hydrolysis of the biomass was favourable. The concentration of the obtained sugars is listed in Table 1 and Figs (3&4).

Table 1: the concentrations of sugars of 1st stage concentrated acid hydrolysis process.

Sample No	Concentration and type of acid used	Dry weight mg	Dissolved dry weight mg	Dissolved dry weight percentage	Xylose mg/ml	Arabinose mg/ml	Galactose mg/ml	Glucose mg/ml	Total dissolved sugars mg/ml	Acetic acid ml
1	10 % H ₂ SO ₄	935	230	24.6 %	6.0	1.0	0	0.5	7.5	0.001
2	10 % HCL	935	314	33.6 %	9.0	1.8	1.2	1.9	13.9	0.006
3	20 % H ₂ SO ₄	935	280	29.9 %	8.0	1.2	0.7	1.8	11.7	0.03
4	20 % HCL	935	320	34.2 %	10.0	2.0	1.3	2.1	15.4	0.04
5	30 % H ₂ SO ₄	935	290	31.0 %	9.0	1.0	0.9	1.7	12.6	0.12
6	30 % HCL	935	380	40.6 %	12.0	2.2	2.0	3.0	19.2	0.13

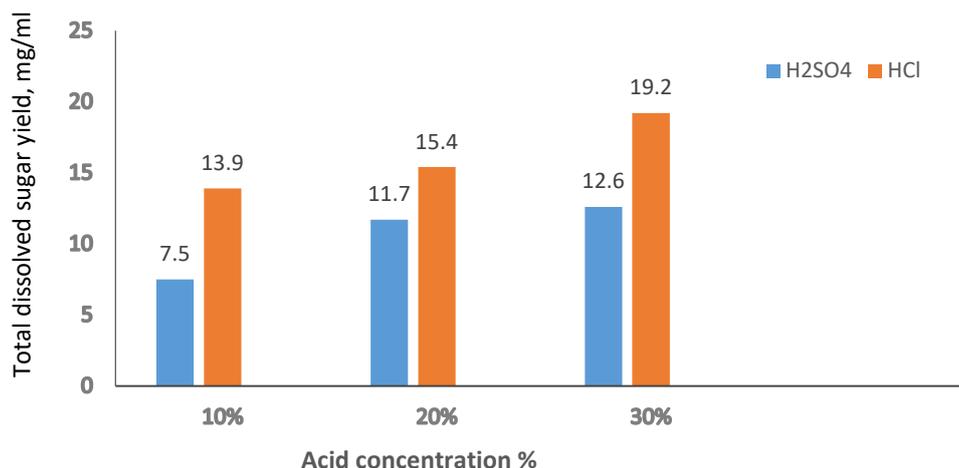


Fig. 3 The first stage dissolved sugar yield (mg/ml) and concentrated acid.

Fig.3 shows the effect of acid concentration and acid type on the total sugar yield. The other parameters such as liquid to solid ratio, temperature, and time and bagasse fibre length for both sulphuric acid and hydrochloric acid were constant. Regarding, Fig 3 it was shown that, as the acid concentration increase, total dissolved sugar increased neglecting

The acid type sulphuric acid or hydrochloric acid, the optimum acid concentration is 30 % in the 1st stage, Also, as shown, hydrochloric acid can dissolve more sugars compared with sulphuric acid under the same acid concentration. Hydrolysis of biomass by hydrochloric acid reaches up to the 1.5 times of the dissolved sugar at 30 % concentration.

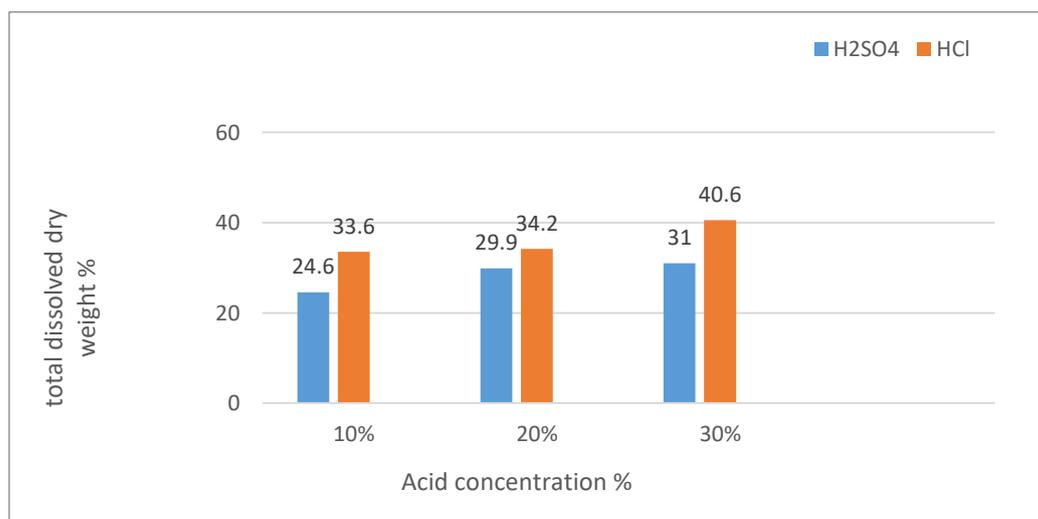


Fig. 4 The first stage total dissolved dry weight % and concentrated acid

Fig. 4 shows total dissolved dry percentage weight with different acid concentrations with two types of acid sulphuric and hydrochloric acid.

The diagram in Fig 4, Indicates that the total dissolved dry weight increased with increasing the acid concentration and also the hydrochloric acid gives results better than sulphuric acid.

3.5.2 Second stage concentrated acid hydrolysis

In the 2nd stage using concentrated acid hydrolysis, the amount of bagasse remained from the 1st stage after hydrolysis was 0.65 gm that reacted with different concentrations of both sulphuric and hydrochloric acid for one hour in a water bath, with moisture content of 4.0 % of the sample and liquid to solid ratio 10:1. Regarding the data that listed in Table 2 and Figs (5&6), the results showed that the

glucose concentration increased from 2.0 to 5.2 mg/ml and xylose also was slightly increased from 1.8 to 2.1 on using H₂SO₄ (20-30%) and total dissolved sugars increased from 4.1 to 8.0 mg/ml. However, on utilization of HCl (20-30%) for the hydrolysis of biomass total dissolved sugars

enhanced from 7.3 to 10.0 mg/ml. The results confirmed that the both acids are acceptable for the hydrolysis process but HCl is beneficially used to hydrolyse biomass with 1.25 to 1.7 times more than sulphuric acid.

Table 2 the concentrations of sugars 2nd stage concentrated acid hydrolysis

Sample No	Concentration and type of acid used	Dry weight mg	Dissolved dry weight mg	Dissolved dry weight percentage	Xylose mg/ml	Arabinose mg/ml	Galactose mg/ml	Glucose mg/ml	Total dissolved sugars mg/ml	Acetic acid ml
7	10 % H ₂ SO ₄	624	32	5.1 %	1.2	0	0.5	0.8	2.5	0
8	10 % HCL	624	45	7.2 %	1.4	0.1	0.9	1.4	3.8	0
9	20 % H ₂ SO ₄	624	51	8.2 %	1.8	0.12	0.13	2.0	4.1	0
10	20 % HCL	624	72.5	11.6 %	2.0	0.16	0.15	5.0	7.3	0
11	30 % H ₂ SO ₄	624	80.5	12.9 %	2.1	0.4	0.3	5.2	8.0	0.001
12	30 % HCL	624	103	16.5 %	2.3	0.9	0.8	6.0	10.0	0.002

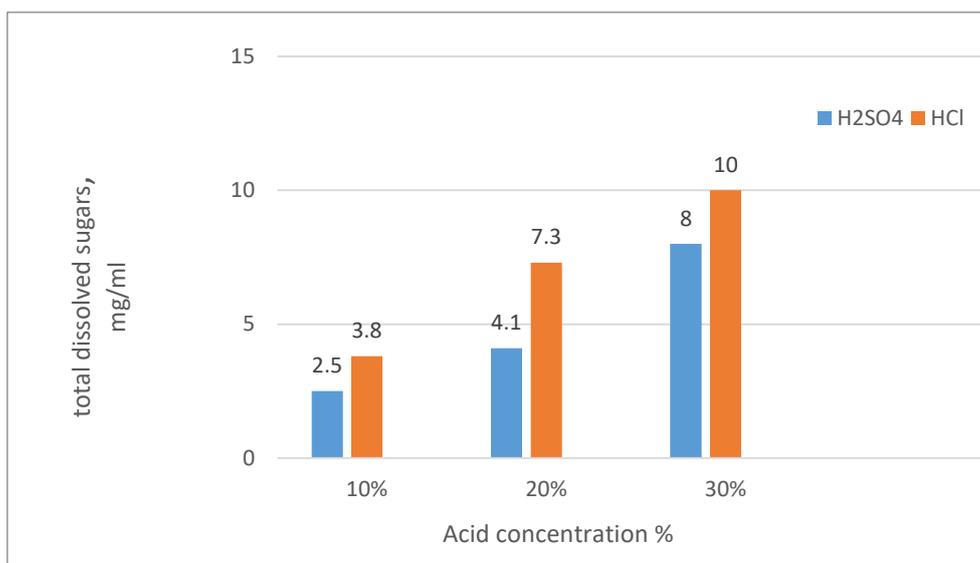


Fig. 5: 2nd stage total dissolved sugars, (mg/ml) and concentrated acid.

Fig 5 shows effect of acid concentration and acid type on the total sugar yield with constant liquid to solid ratio, temperature, and time and bagasse fibre length for both sulphuric acid and hydrochloric acid.

In Figs 5&6 the chart clear that, the hydrochloric acid is more effective in the biofuel hydrolysis more

than sulphuric acid in the second stage of concentrated acid hydrolysis process. Fig 6 shows Total dissolved dry weight with different acid concentrations with two types of acid used, sulphuric and hydrochloric acid.

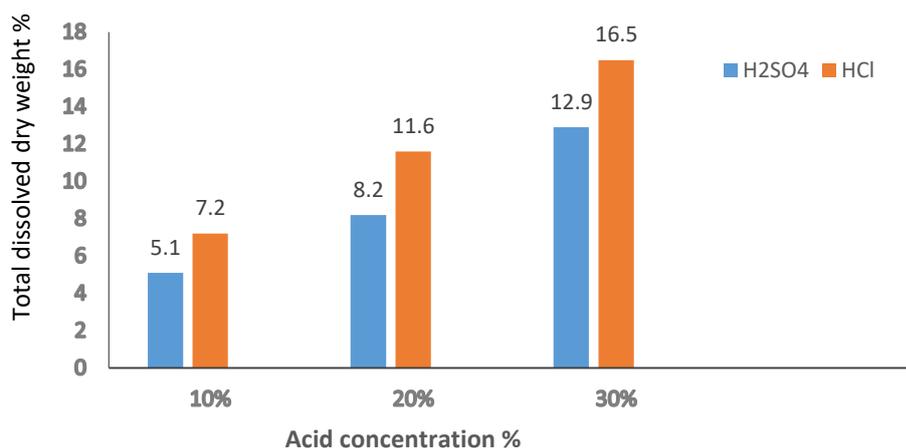


Fig 6: 2nd stage total dissolved dry weight % versus acid concentration.

4. Conclusions

Hydrochloric acid is more effective and powerful than sulphuric acid with the same concentration in the biofuel hydrolysis process, the yield of the dissolved sugar is more than sulphuric acid. For both stages of the concentrated acid hydrolysis process. Also the recovery of the hydrochloric acid after the concentrated acid hydrolysis process will be cheap and easy more than the recovery of the concentrated sulfuric acid according to the low boiling point of the hydrochloric acid comparable with the high boiling point of the sulfuric acid which lead to more energy consumption and increase the total operation cost

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