

**INTENSIFICATION AND OPTIMIZATION OF
HETEROGENEOUS CATALYZED HYDROLYSIS OF
LIGNOCELLULOSIC BIOMASS**

THESIS

Submitted by

SOURAV BARMAN

[Exam. Roll No.M4CHE1607]

[Class Roll No. 001410302012]

[Reg. No. 128886 of 2014-2015]

Under the Guidance of

Dr. Rajat Chakraborty

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Declaration of originality and compliance of academic ethics

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his “*Master of Chemical Engineering*” studies.

All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

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Name: **Sourav Barman**

Examination Roll Number: **M4CHE1607**

Thesis Title:

Intensification and Optimization of Heterogeneous Catalyzed Hydrolysis of Lignocellulosic Biomass

Signature:

Date:

MAY 2016

CERTIFICATION

This is to certify that Mr. Sourav Barman, final year Master of chemical Engineering (M.E) examination student of Department of Chemical Engineering, Jadavpur University (Exam Roll:M4CHE1607; Regd. No.:128886 of 2014-2015), has completed the Project work titled

“Intensification and Optimization of Heterogeneous Catalyzed Hydrolysis of Lignocellulosic Biomass” under the guidance of Dr. Rajat Chakraborty during his Masters Curriculum. This work has not been reported earlier anywhere and can be approved for submission in partial fulfillment of the course work.

Prof. (Dr.) Chandan Guha
*Head of Department and Professor,
Chemical Engineering Department
Jadavpur University.
Jadavpur University.*

Dr. Rajat Chakraborty
*Project Supervisor,
Associate Professor,
Chemical Engineering Department*

Prof. Sivaji Bandyopadhyay
*Dean of Faculty and Engineering
Technology
Jadavpur University.*

DEDICATION

*Special Dedication to my parents, friends and my
respected project supervisor*

For all your care, support and believe in me.

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CHAPTER-1

ABSTRACT

1. Abstract:

This is the first report on experimental and heterogeneous kinetic simulation on waste papaya (*Carica Papaya*) peel hydrolysis for glucose synthesis. The effects of far infrared (FIR) radiation on pretreatment and subsequent hydrolysis in one-pot system using Amberlyst-15 catalyst have been optimized. Respective optimal values of process parameters in one-pot pretreatment and subsequent hydrolysis were viz. 70°C and 80°C, reactor temperature, 20 min and 10 min batch time, water to biomass ratio (w/w) of 5 and 20, NH₄OH loading (w/w) of 2.5 and catalyst concentration (wt. %) of 7.5 corresponding to the maximum 88.21 mol% glucose yield using far infrared radiated reactor (FIRRR). The glucose yield about two times greater than that obtained through conventionally heated stirred batch reactor (CHSBR) (36.42 mol %). Eley-Rideal mechanism was best fitted with the hydrolysis kinetics compared to Langmuir-Hinshelwood and pseudo-homogeneous models. Significantly, the FIRRR consumes approximately 1/3rd energy of CHSBR (68.25 kJmol⁻¹) owing to lower activation energy (16.27kJmol⁻¹) under FIR radiation.

CHAPTER-2

INTRODUCTION

2. Introduction:

Amongst all the sovereign countries, India generates 1 million tons of solid wastes per day due to lack of awareness regarding solid waste disposal thus rendering environmental and ecological disturbances. So, it is an utmost need to mitigate such disposal problem by enacting proper solid waste management policy. Hence, researchers are focusing on the utilization of the solid waste for generation of value added chemicals viz. fermentable sugars, propanol, furfural, 5-hydroxymethyl furfural and bioethanol in a sustainable and economic pathways.

Therefore, there is an utmost necessity to utilize the biomass through a sustainable hydrolytic route. This not only meets the increasing energy crisis of the recent world that has led the researchers to explore an alternative renewable resource.

Biomass specifically lignocellulosic biomass (LB) is available all over the world and it has been generated in tons from organic materials such as agricultural crops and their residues and daily household wastes.

2.1. Lignocellulosic Biomass and its Resources:

Several tons of waste biomass is getting accumulated day by day which has raised the concern of environmentalists to find out a better management policy that will mitigate the existing problem. LB resources seem to be the most abundant and thus researchers are trying to reduce, reuse and recycle this LB to generate bio fuel and value-added chemicals. LB includes industrial wastes, municipal wastes, energy crops, wood and agricultural residues. Biomass availability in India has been summarized in **Table 2.1** to understand the present scenario.

2.1.1. Lignocellulosic Industrial and Municipal Waste:

Industrial and municipal waste management has both economic and environmental implications which should be considered also for biofuel production (*Kalogo et al. 2007; Chester et al., 2009*). Cellulosic materials from industrial and municipal wastes consisting of paper, cardboard, kitchen waste, could be converted into biofuel (*Li et al., 2007*), though these are not an ideal feedstock, because of contaminations in miscellany industrial and municipal wastes components. Nevertheless, the biodegradable organic fractions which contain lignocellulose could be used as potential raw materials.

2.1.2. Lignocellulosic Agricultural Waste:

Agricultural crop residues generated from both harvesting and processing of crops are abundant and renewable resources. It generally contains more hemicellulosic material than woody biomass (approximately 25-35%) (*Demirbas et al., 2005*). Apart from an ecofriendly, uses of agricultural residues also help to avoid dependence on forest woody biomass and thus reduce deforestation. Agricultural crop residues are generally straw and stalks, leaves, seed pods which are left as field residues and husks, seeds, bagasse, roots left after the processing of the crop. In terms of availability of biomass rice straw, wheat straw, corn stover, and sugarcane bagasse are the foremost agricultural wastes (*Kim et al., 2004*) among which Sugarcane is the main agricultural crops cultivated in India.

2.1.3. Lignocellulosic Forestry Wastes:

Residues from natural forest, forestry wastes are the main sources of waste woody materials such as sawdust, dead trees, and cultivated first growing energy tree species. There are two kinds of forest woody materials available as LB feedstock based on density and duration of growth, softwoods and hardwoods (*Hoadley et al., 2000*). Softwoods produced by conifers and

gymnosperm trees (*Sanchez et al., 2008*) which involve evergreen species viz. pine, cypress, spruce, fir, cedar, hemlock, and redwood whereas hardwoods include trees such as poplar, willow, oak, cottonwood, and aspen. Woody biomass possesses certain advantages over agricultural plants in terms of flexibility in harvesting, less ash content and transportation ease due to thick secondary wall.

Table 2.1: Lignocellulosic Biomass availability in India

Lignocellulosic Resources	Availability (Mt/year)	Reference
Municipal waste	>68.8	<i>Sharholly et al., 2008; Pappu et al., 2007</i>
Agricultural waste	>350	<i>Pappu et al., 2007</i>
Forestry waste	>321	<i>Sudha et al., 1999; Sudha et al., 2003</i>

2.2. Constituents of Lignocellulosic Biomass and its Properties:

Composition of LB plays a very important role in the performance and efficacy of both pretreatment and hydrolysis stages. This dry waste plant material is generally made of three main components viz. cellulose, hemicellulose and lignin which vary from plant to plant (**Table 2.2**). The carbohydrate polymer components (cellulose, hemicellulose) of biomass cell wall were surrounded by an aromatic polymer component (lignin). Besides these three main components, some other substances such as extractives (e.g. phenolic constituents terpenoids) (*Sjöström et al., 1993*), ashes and pectin were also present in the cell wall.

Cellulose is a homogeneous polysaccharide derived from glucose units which are connected through β -1, 4-glycosidic bonds. It is a linear polymer with a degree of polymerization (DP) up to 15,000 (*Bodřiláu et al., 2007*). The crystalline cellulose structure is formed due to its high molecular hydrogen bonding which is actually hindering the catalysts access during the hydrolysis process. The natural form of cellulose is cellulose I with two different crystal phases Cellulose I_α and cellulose I_β . Cellulose I_α is less stable than cellulose I_β as the later one can be reversibly converted by heating treatment. These two crystal phases, I_α and I_β varies depending on the species (*Hayashi et al., 1997; Wada et al., 2006; Chundawat et al., 2011*).

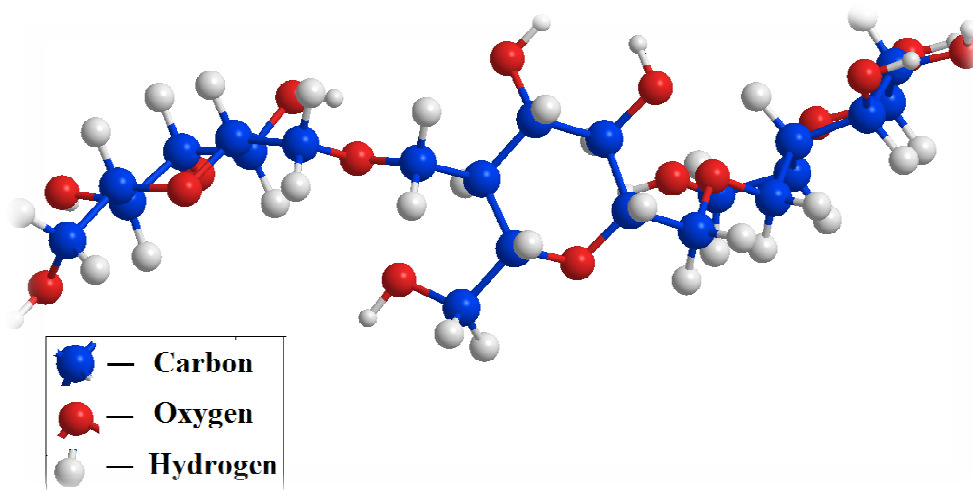


Figure 2.2 (a): 3D structure of cellulose

Hemicellulose is another carbohydrate polymer component in biomass cell wall but unlike cellulose it is a heterogeneous polysaccharide. Its DP is normally around 200 and it is a mixed branched polymer of pentoses (xylose, arabinose), hexoses (glucose, mannose and galactose) and sugar acids (D-glucuronic acid, D-galacturonic acid) (*Ragauskas et al., 2006; Harmsen et al., 2010; Zhao et al. 2012*). Hemicellulose connected with cellulose microfibrils via hydrogen bonds and lignin is connected to hemicellulose by covalent bonds (*Faulon et al., 1994*).

Hemicellulose is hydrophilic in nature and furthermore, it has random, amorphous structure, which makes it easily hydrolysable component than cellulose. Like, cellulose its composition and structure also varies depending upon the species such as stem, branches, roots and barks (*Sjöström et al., 1993*).

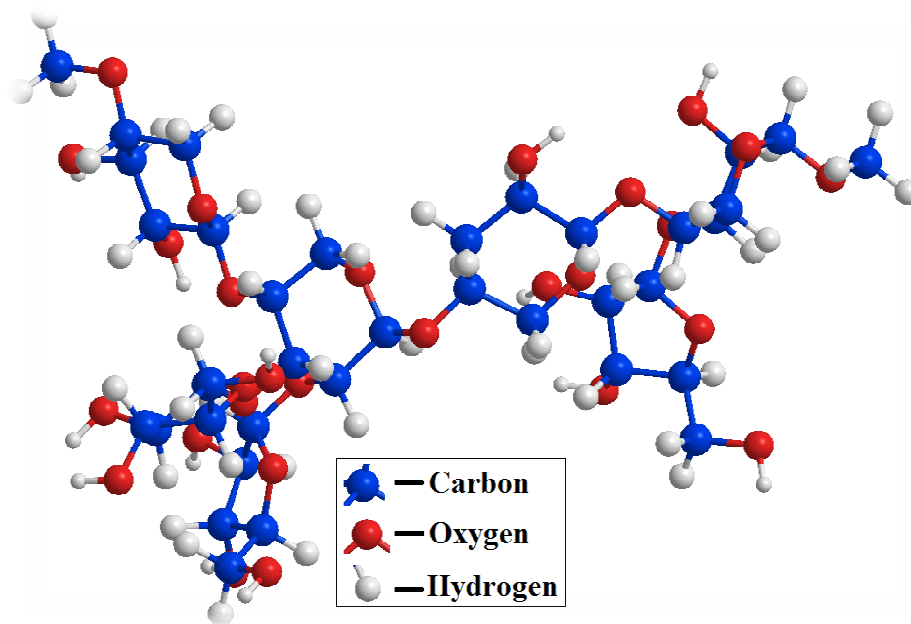


Figure 2.2 (b): 3D Structure of hemicellulose

Lignin is a three dimensional aromatic polymer of monolignols (aromatic alcohols). The three main monolignols viz. coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol; are the fundamental building blocks of lignin which are vary among different species (*Ramos et al., 2003; Whetten et al., 1998*). Generally, lignin in grasses contents all three monolignols units whereas lignin in softwood is primarily contains coniferyl alcohol units (95%). In hardwood lignins both coniferyl alcohol units and sinapyl alcohol units are present in different ratios (*Buranov et al., 2008; Chundawat et al., 2011*). The ether, ester and glycosidic linkages between lignin and carbohydrates give the physical strength to plant tissue (*Sjöström et al.,*

1993). Lignin acts as a protective barrier that prevents plant cell destruction. So, it must be broken down for easy access of cellulose for the hydrolysis conversion.

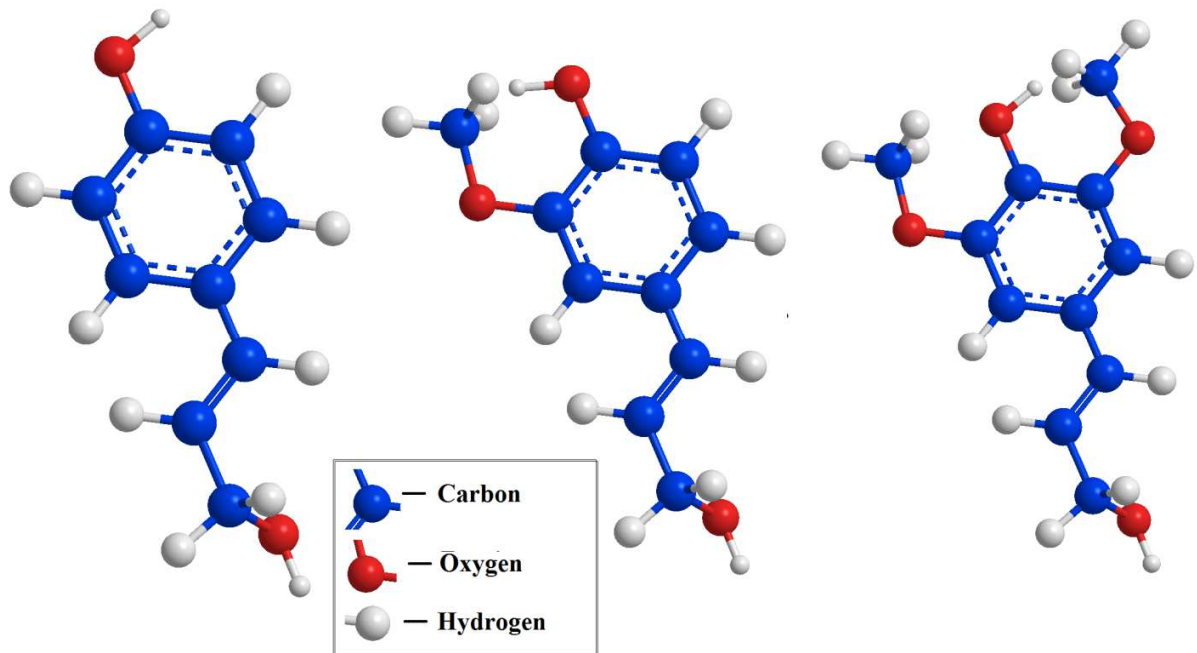


Figure 2.2 (c): 3D Structure of three building blocks of lignin: (a) P-Coumaryl
(b) Coniferyl (c) Sinapyl

Table 2.2: Different LB resources and its composition (g/100 g of dry matter)

Lignocellulosic Biomass		Cellulose (%)	Hemicellulose (%)	Lignin (%)
Municipal Waste (Das et al., 2010; Hadar et al., 2013)	Banana peel	1.3	3.83	0.93
	Tomato	9.1	11	5.3
	Oat seed	11.9	-	-
	Potato peel	1.2	9.2	-
	Paper	85.0-99.0	0.0	0.0-15.0
	Waste Papers from Chemical Pulps	60.0-70.0	10.0-20.0	5.0-10.0

	Newspaper	40.0-45.0	25.0-40.0	18.0-30.0
	Primary wastewater solids	8.0-15.0	0.0	24.0-29.0
Agriculture Waste <i>(Mood et al., 2013; Hadar et al., 2013)</i>	Wheat Straw	35.0-39.0	23.0-30.0	12.0-16.0
	Barley Hull	34.0	36.0	13.8-19.0
	Barley Straw	36.0-43.0	24.0-33.0	6.3-9.8
	Rice Straw	29.2-34.7	23.0-25.9	17.0-19.0
	Rice Husks	28.7-35.6	12.0-29.3	15.4-20.0
	Oat Straw	31.0-35.0	20.0-26.0	10.0-15.0
	Ray Straw	36.2-47	19.0-24.5	9.9-24.0
	Corn Cobs	33.7-41.2	31.9-36.0	6.1-15.9
	Corn Stalks	35.0-39.6	16.8-35.0	7.0-18.4
	Sugarcane Bagasse	25.0-45.0	28.0-32.0	15.0-25.0
Sorghum Straw	32.0-35.0	24.0-27.0	15.0-21.0	
Softwood <i>(Hadar et al., 2013)</i>	Pine	42.0-50.0	24.0-27.0	20.0
	Douglas fir	44.0	11.0	27.0
	Spruce	45.5	22.9	27.9
Hardwood	Poplar	50.8-53.3	26.2-28.7	15.5-16.3
	Oak	40.4	35.9	24.1
	Eucalyptus	54.1	18.4	21.5
Grasses	Grasses	25.0-40.0	25.0-50.0	10.0-30.0
	Switchgrass	35.0-40.0	25.0-30.0	15.0-20.0

2.3. Valuable chemicals from LB and its applications:

As mentioned earlier, LB is the most promising renewable resource with great potential for viable production of biofuels and value-added chemicals. Various LB feedstocks can be processed to a range of biorefinery streams called platforms which includes six carbon sugars derived from cellulose; a mixed five or six carbon carbohydrates from hemicellulose, lignin and organic solutions from grasses. These primary platforms can be further treated to produce a wide range of marketable chemical products using the arrangements of thermal, chemical and biological process.

The sugar derived from cellulose is glucose which is further converted into valuable products viz. ethanol, propanol, lactic acid, succinic acid, acetone, butanol and butandiol while both glucose as well as the other six (mannose, rhamnose, galactose) and five (xylose, arabinose) membered sugars can be produced by hydrolyzing the hemicellulose (*Werpy et al., 2004*).

Besides polysaccharides, conversion of lignin also has promising potential and it can be considered as most abundant component in the LB for production of aromatic compounds. Recently, several studies have been investigated to convert the lignin into more versatile products such as fuel additives. Currently lignin is used as road binder, concrete admixture, dye dispersant, vanillin production, oil well drilling mud, animal feed pellets, pesticide dispersant and solid fuel for combustions (*Bozell et al., 2007*).

The fermentation products such as ethanol and acetone, butanol will allow several derivative products to capture new and increased market shares. Their conversion products such as ethylene, ethylene glycol, vinyl chloride, propene and butadiene have made a great impact on polymer chemistry (*Ezeji et al., 2007*). Lactic acid is also considered as a useful fermentative

product due to its biofunctionality and it can be further converted to many reaction compounds viz. acetaldehyde, propanoic acid, acrylic acid, dilactide and 2,3-pentanedione (*Ruiz et al., 2010*).

The other chemical transformation products are sorbitol, furfural, glucaric acid, hydroxymethylfurfural and levulinic acid derived from the platform chemicals by selective dehydration, oxidation and hydrogenation process. Sorbitol is used as a food ingredient, personal care ingredient (e.g. toothpaste) and also for industrial use (*Zhang et al., 2013*). Furthermore, Furfural is used as raw material for Nylon 6 and Nylon 6,6 whereas as a lubricant, softener and chemical HMF is used (*Yoshida et al., 2008*). Another useful chemical, Levulinic acid produced from hydrolysis of carbohydrates is used as plasticizer, resin, textile, animal feed, coating and as antifreeze (*Leibig et al., 2010; Ertl et al., 2014*).

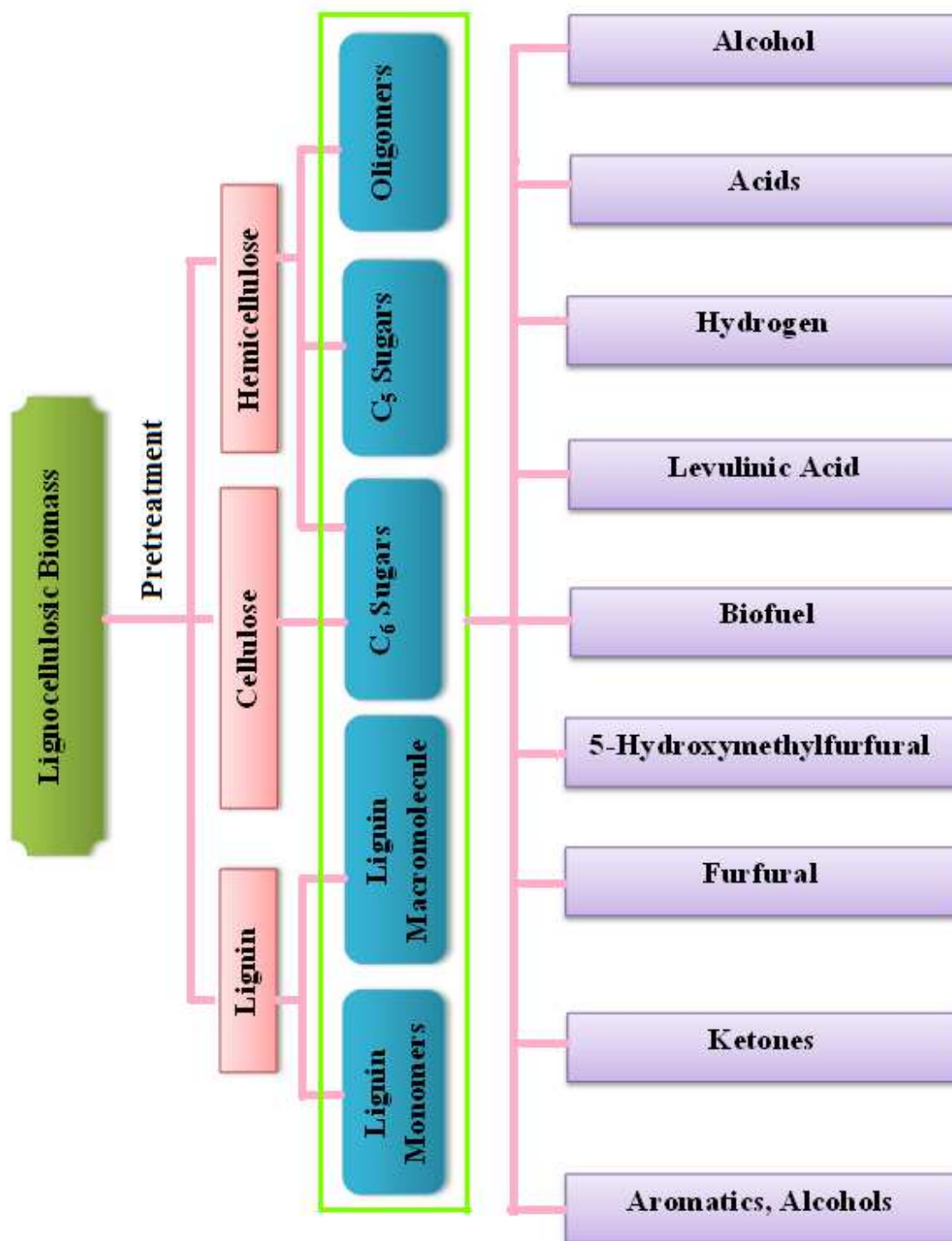


Figure 2.3: Value added chemicals derived from LB

2.4. Importance and Utility of present work:

In India papaya peel is abundantly available biomass which contains large amount of cellulose (60-80 wt. % of cellulose and 4-6 wt. % of lignin) (*Vikas et al., 2014*) indicating a great potential as feedstock for hydrolytic conversion into valuable products. Waste papaya peel (WPP) usually contains appreciable amount of glucose. *Patidar et al., 2016* reported valorization of waste papaya peel for production of acidic pectin methylesterase by *Aspergillustubingensisth* at 50 °C and pH 4.6. *Wankasi et al., 2011* produced furfural from ripe papaya peel by acid hydrolysis. *Kamaruzzaman et al., 2005* reported the use of dried papaya peel as a nutritional ingredient for broiler chickens. *Sittiruk et al., 2006* reported the extraction of proteolytic enzyme from papaya latex which can be used for hydrolysis purpose of raw hide. Evidently the literature review reveals that no research has been reported on papaya peel hydrolysis for glucose production in spite of presence of high amount of cellulose.

The first report on the hydrolysis kinetics of LB lignocellulosic biomass such as wood was delineated as pseudo-first order homogeneous consecutive series reactions by *Saemens et al., 1945*. Subsequently Several reports (*Aguilar et al., 2002; Chong et al., 2004; Kumar et al., 2015*) on pseudo-homogeneous (PH) hydrolysis kinetics of fruit/food wastes, viz., sugar cane bagasse has been observed. However, in all the mentioned works, the initial sugar content in the biomass feedstock was not considered. To the best of our knowledge no report is available in scientific literature considering initial concentration of glucose in evaluation of hydrolysis kinetics of WPP and similar other fruit waste/vegetable wastes (*Vendruscolo et al., 2008; Cekmecelioglu et al., 2005*).

From literature review it is evident that no work has been reported on WPP hydrolysis for glucose synthesis. This article investigates on optimization of pretreatment and subsequent hydrolysis of pretreated waste papaya peel (PWPP) for maximization of glucose yield through one-pot (*Matson et al., 2011; Kobayashi et al., 2013*) conversion in energy-efficient far infrared radiated reactor (FIRRR). The parametric conditions of pretreatment and hydrolysis were optimized using Taguchi orthogonal design (TOD). The superiority of FIRRR over that of conventionally heated stirred batch reactor (CHSBR) in the one-pot batch glucose synthesis process has been evaluated. At optimal process condition, novel pseudo-homogeneous pseudo-first order (PHPF) hydrolysis kinetic model has been developed by modifying the conventional model (*Aguilar et al., 2002*) through consideration of initial glucose concentration in the PWPP.

CHAPTER-3

LITERATURE REVIEW

3. Literature Review:

3.1. Hydrolytic Transformation of LB:

Transformation of LB into value added chemicals involves mainly three crucial steps viz. pretreatment, hydrolysis and fermentation. Initially, physical treatment of biomass feedstocks is done followed by other chemical/physicochemical/biological pretreatment process to break the crystalline structure of biomass and enhance the accessibility of cellulose component. After pretreatment, the pretreated biomass is hydrolyzed by either enzymatic or catalytic hydrolysis process which is further processed to produce value added products by fermentation process.

LB hydrolysis process, which involves breakdown of β -1,4-glycosidic linkage of cellulose is an important step for cellulose conversion. So far, the hydrolysis process is not economically feasible at an industrial scale due to its low economy and efficiency. Although extensive research work has been carried out to improve the hydrolysis process, the efficient conversion of carbohydrate in LB into the reducing sugar is still a headache. Hydrolysis of LB can be achieved by either enzymatic or catalytic hydrolysis process. A number of enzymes like cellulase, β -glucosidase, xylanase showed important roles in enzymatic hydrolysis and for catalytic hydrolysis, several liquid inorganic or organic acids and solid acids such as sulfonated carbon, heteropoly acids, zeolites and oxides. Recently, *Jin et al., 2016* performed an experiment using cellulase enzyme for hydrolysis of *Catalpa* sawdust. Furthermore, the results showed that using thermo- $\text{Ca}(\text{OH})_2$ pretreatment the sugar yield was increased up to 1185.7% at optimized condition. Since last few decades, uses of different enzymes mixture in the cellulosic hydrolysis process also have been broadly studied (*sun et al., 2002; Excoffier et al., 1991; Xin et al., 1993*). For instance, a mixture of β -glucosidases with *T. reesei* cellulases system achieved better saccharification than for the system without β -glucosidases (*Excoffier et al., 1991; Xin et al.,*

1993). Though enzymatic hydrolysis resulted in considerably high amount of sugars, still it has some drawbacks viz., high reaction time, difficulties in product separation and reusability and high cost of enzyme.

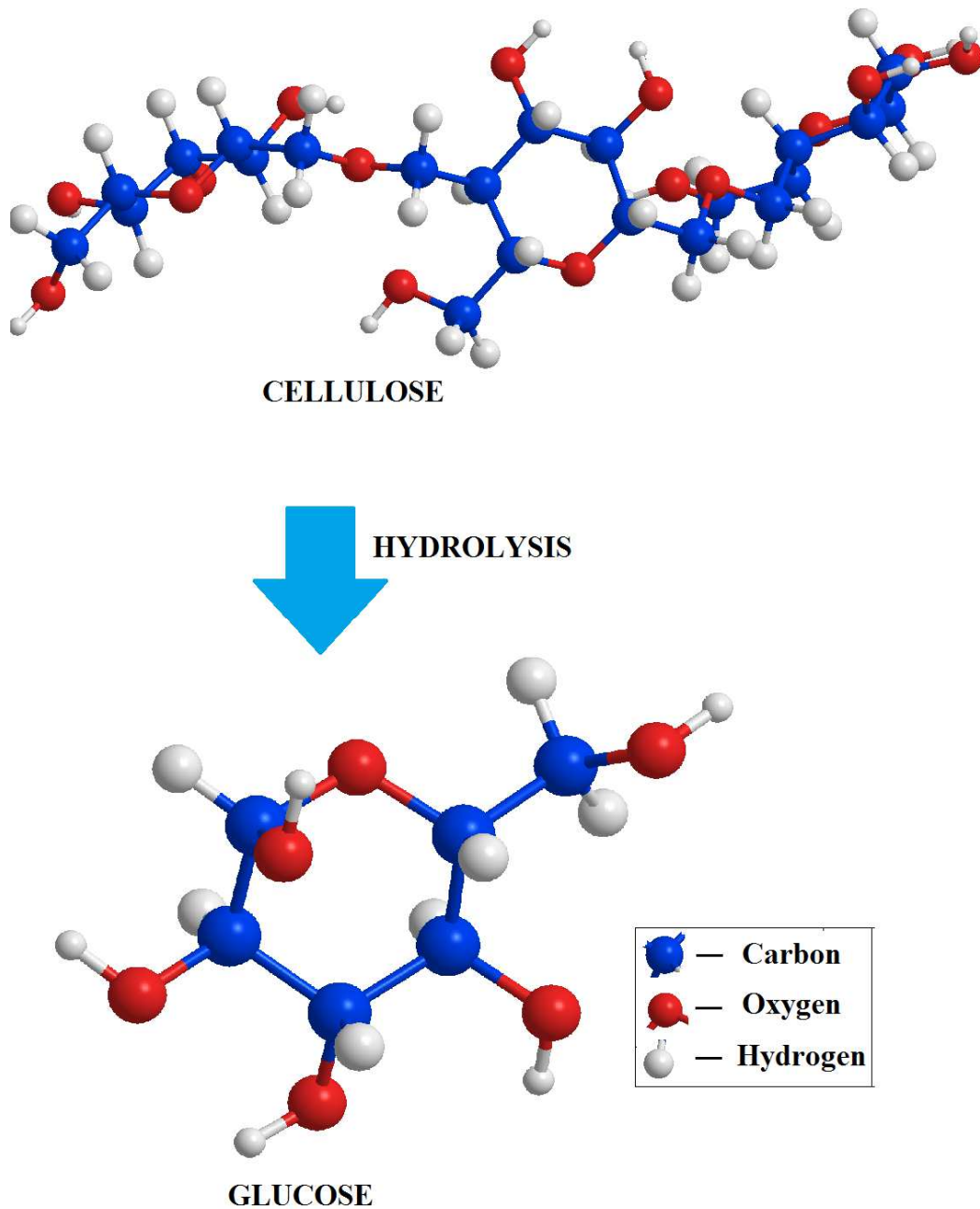


Figure 3.1: schematic diagram of hydrolytic conversion of cellulose into glucose

3.1.1. Direct Hydrolysis:

Hydrolysis of LB without pretreatment can be achieved by using acid catalyst as they have the capability to penetrate the cellulosic structure which results swelling of cellulose and breakage of glycosidic bonds. Several research works have been reported on direct hydrolysis of LB using mineral acids (*Kupiainen et al., 2012; Park et al., 2013; Zhou et al., 2014*) which suggested that two different approaches are commonly applied for direct hydrolysis process viz. dilute acid and concentrated acid hydrolysis. Dilute acids with high reaction temperature and pressure for hydrolysis of biomass is the oldest method. Though dilute acids can disrupts the cellulosic structure, several disadvantages such as lower product yield, high energy consumption are associated with this process. To overcome this, concentrated acids are introduced. For instance, the effect of H₂SO₄ concentration (31-70%, (w/v)) on microcrystalline cellulose hydrolysis was investigated by *Camacho et al., 1996*. He reported that total cellulose solubilization of was achieved when acid concentration was above 62% (w/v). Furthermore, to understand the efficacy of acids catalysts in direct biomass hydrolysis process, recently *Hilpmann et al., 2016* performed an experiment to hydrolyze xylan using several mineral acids (HCl, H₂SO₄, trifluoroacetic acid, oxalic acid) and a solid acid catalysts (Smopex-101) with varying the pH value (0.5-3) at moderate temperature (70-90°C). The results showed that maximum xylan conversion can achieved when the pH value of the homogeneous catalysts were lower than 2. However, concentrated acid hydrolysis process also has some disadvantages such as corrosion and recovery issues as mentioned previously and strict requirements on water content of raw materials. In last few years, two-stage hydrolysis process for biomass conversion has been introduced for successively hydrolyzed the hemicellulose and cellulose portion to produce better sugar yield. *Yoon et al., 2014* has performed a two-step concentrated sulfuric acid

process for hydrolysis of cotton. The result showed that, severe degradation of sugar was occurred at higher reaction temperature (100-120°C) in second hydrolysis step. He also reported that, to maximize glucose yield, reaction temperature should keep at 100°C in second hydrolysis step.

3.1.2. Pretreatment Before Hydrolysis:

In order to enhance accessibility of cellulose for effective hydrolysis of LB pretreatment before hydrolysis process is required. Since the last few decades, several pretreatment methods have been studied which are broadly classified into four categories viz. physical (milling, grinding), chemical (alkaline, acid, wet oxidation, organic solvent, oxidizing agent), physicochemical (steam explosion, super critical fluid, liquid hot water, ammonia fiber explosion) and biological pretreatment.

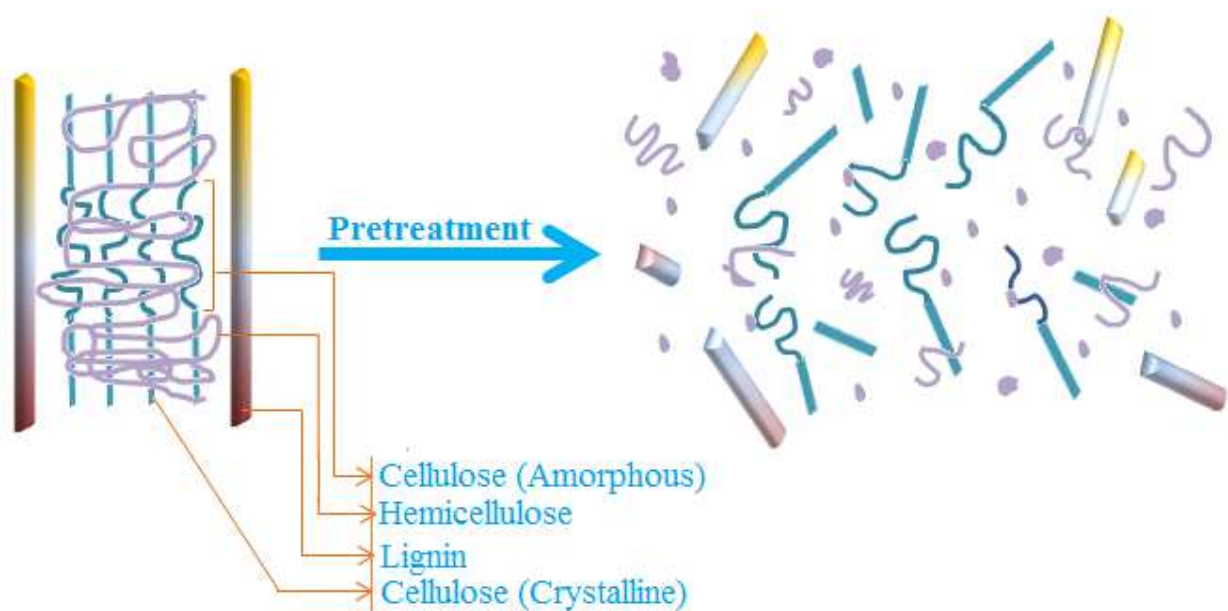


Figure 3.1.2: Schematic representation of LB pretreatment

The above-mentioned pretreatment process can be used to remove lignin and hemicellulose part, reduce the crystallinity of cellulose and increase the surface area with the aim of rapid conversion of carbohydrate portion to monomeric sugars with greater yields.

3.1.2.1. Physical pretreatment:

The physical pretreatment process is performed by milling or grinding process which reduces biomass crystallinity through breakdown of biomass size. The reduced biomass size increases the mass transfer characteristics as it increases the surface area which in turns improved the hydrolysis rate. The required energy for physical pretreatments depends on the final reduced biomass size which is greater than the theoretical energy content available in the biomass.

3.1.2.2. Chemical pretreatment:

i. Alkaline pretreatment:

The chemical pretreatment of LB can be done by alkaline pretreatment method by using bases viz. sodium, potassium, calcium and ammonium hydroxide. In this pretreatment process, effective alteration of lignin is occurred as alkali causes degradation of ester and ether linkage which enhances the accessibility of hemicellulose and cellulose to the catalysts.

Sodium, calcium and potassium hydroxide generally employed for the pretreatment of low lignin content biomass such as softwood and grasses. These pretreatment processes, cause low sugar degradation and prevent lignin condensation which increases lignin solubility (*Sharma et al. 2012*). The effect of lime (calcium hydroxide) pretreatment on rice hulls for ethanol production was investigated by (*Saha et al., 2008*). They found that the maximum sugar yield was 12.6% resulted at optimal condition of 121°C and 1h pretreatment time at 100 mg

lime/g hulls. Similarly, (*Kim et al., 2005*) also studied the pretreatment effect on corn stover using excess lime (0.5 g Ca(OH)₂/g raw biomass) at different temperature in both oxidative and non-oxidative conditions. The maximum xylose and glucose yield of 79.5% and 93.2% respectively were achieved, when corn stover was hydrolyzed with 15 FPU/g cellulase for 4 weeks at 55 °C with aeration. The effects of sodium hydroxide for pretreatment of switchgrass, wheat straw, hardwoods and softwoods with lignin content less than 26% has been studied by *Zhao et al., 2008*. *Zhu et al., 2010* also showed that production of biogas from corn stover was increased by 37% compared to that of untreated cellulose. Similar to the above study, potassium hydroxide (KOH) effect on switch grass was investigated by (*Sharma et al., 2012*). It was observed that around 99.26 % sugar retention was occurred at 21 °C and after 12 h treatment at 0.5 % KOH.

As it has been clearly observed from the present study, that alkaline pretreatment process involving calcium, sodium and potassium hydroxides were highly effective for biomass conversion, however, efforts must be made to overcome several drawbacks such as high downstream processing costs, utilization of huge amount of water for washing salts of calcium and sodium, formation of inhibitors.

ii. Wet oxidation:

In this pretreatment process, oxygen is used to oxidize the LB which involves both low and high temperature reactions. It is used to separate the lignocellulosic compound by removing lignin and solubilizing hemicellulose. During this oxidation process, lignin is oxidized to carbon dioxide, carboxylic acids, water and approximately 50% to 70% lignin removal can be achieved after the pretreatment depending upon the biomass type and pretreatment conditions used (*Bjerre et al.,*

1996; *Martín et al., 2007; Banerjee et al., 2009*). Effect of wet oxidation pretreatment of sugarcane bagasse at several pretreatment conditions was investigated by *Martín et al., 2007*. The result showed that at pretreatment conditions of 195 °C and 15 min 40–50% of lignin and 93–94% of hemicelluloses were solubilized, while at 185 °C, 5 min and alkaline pH only 20% of lignin and 30% of hemicelluloses were solubilized. In combination with other pretreatment methods, wet oxidation pretreatment can be used to enhance the biomass conversion process (*Schmidt et al., 2002; Georgieva et al., 2008; Sørensen et al., 2008*). For instance, wet oxidation with alkaline pretreatment can reduce the byproducts formation, thus decreasing inhibition (*Martín et al., 2006*) whereas in addition with steam explosion, this process has the capability to process larger particle sizes and to work at higher substrate loadings, up to 50% substrate (*Georgieva et al., 2008*). Furthermore, a comparative study between the effect of steam explosion and wet explosion on sugarcane bagasse has been investigated by (*Martín et al., 2008*). It is observed that after pretreatment over a time span of 15 min, 50% of lignin was removed in wet explosion process whereas only 35% lignin was discharged in case of steam explosion, under the same pretreatment conditions.

iii. Acid pretreatment:

Both diluted and concentrated acids can be used for acid pretreatment of LB. Dilute acid pretreatment operates at elevated temperature whereas concentrated acid pretreatment operates under low temperature condition. Various research works have been reported on acid pretreatment on different biomass, among which sulfuric acid (H₂SO₄) is the most commonly used acid. Sulfuric acid pretreatment mainly used to hydrolyze hemicellulose into xylose which further converted into furfural (*Zeitsch et al., 2000*). *Cara et al. 2008* studied the effects of dilute

sulfuric acid on thin branches and leaves of olive tree biomass at various acid concentrations (0.2–1.4 %) and temperatures (170–210°C). At optimized pretreatment condition of 170°C temperature and 1.0 % acid concentration, maximum 48.6 % sugar yield was observed. Other pretreatment process using acids viz. hydrochloric acid (HCl)(*Wang et al., 2014*) nitric acid (HNO₃) (*Himmel et al., 1997*), oxalic acid (*Kundu et al., 2015*) and phosphoric acid (H₃PO₄) (*Zhang et al., 2007; Marzioletti et al., 2008*) have also been investigated since last few decades. Effects of oxalic acid in pretreatment process were investigated by *Lee et al., 2013* using waste medium after cauliflower mushroom as biomass. The enzymatic conversion of this pretreated biomass results glucose yields up to 77.63%. *Avci et al., 2013* also studied effects of another acid (dilute H₃PO₄) in pretreatment of corn stover for furfural production. Result showed that maximum 61.6% furfural yield was attained at optimal temperature of 200°C and optimal time of 20–25 min. Owing the capability to effective removal of hemicellulose (*Kimet al., 2012; Sun et al., 2016*); it can be considered to use with alkali pretreatment for pure removal of cellulose.

iv. Organosolv Pretreatment:

Organic solvent viz. acetone, ethanol, methanol, ethylene glycol can be used for lignin extraction from LB (*Ichwan et al., 2011*). Due to some serious drawbacks such as environmental pollution, uses of hazardous chemicals, problem in product separation associated with conventional pretreatment process, organosolv pretreatment process can be considered more feasible for lignocellulosic biorefinery process. In this pretreatment process, breakdown of the interior lignin bonds and as well as the bonds between hemicellulose and lignin was occurred at an elevated temperature (150–200°C) (*Ghose et al., 1983*). However, in addition with acid

catalysts this pretreatment process can be conducted under milder condition (*Chum et al., 1985*). As a catalyst, in organic solvent pretreatment process several mineral acids such as sulfuric, hydrochloric and phosphoric acids and organic acids such as oxalic, salicylic, and acetylsalicylic acids can be used (*Sun et al., 2002*). *Ichwan et al., 2011* separated cellulose from oil palm pulp using several solvents such as ethanol–water, ethylene glycol–water and acetic acid–water mixture. The extracted cellulose yield was reached to 41.7; 48.1 and 50.1% by using acetic acid–water mixture, ethanol–water and ethylene glycol–water, respectively. Furthermore, it was found that, acetic acid–water mixture pulping offered maximum cellulose degradation whereas ethanol–water mixture pulping offered higher crystalline cellulose (68.67), followed by ethylene glycol–water mixture as (58.14) and acetic acid–water mixture as (54.21). In organosolv pretreatment process, the lignin and hemicellulose portions are dissolved in the solvent as liquid and cellulose is recovered as solid which overcome the problems related to product separation. For instance, organosolv pretreatment of wheat straw using crude glycerol was conducted by *Sun et al., 2008* reported up to 70% of hemicellulose and 65% of lignin removal were achieved whereas 98% cellulose retention was achieved at optimized pretreatment condition. Though organosolv pretreatment process has been extensively utilized for effective extraction of lignin, it has also some drawbacks such as high solvent and catalysts cost, inflammable organic solvents.

v. *Ozonolysis pretreatment:*

It is another chemical pretreatment process, in which ozone is used for treatment of LB. This pretreatment process generally involves lignin disruption by ozone which attacks the lignin aromatic rings structures, whereas the structure of hemicellulose and cellulose remain unchanged (*Nakamura et al., 2004*). In such pretreatment process, lignin is converted to acids, which have

to be removed for enhancing the subsequent hydrolysis and fermentation process (*Hammel et al., 2002; Alvira et al., 2010*). Pretreatment of wheat and rye straws with ozone to enhance enzymatic hydrolysis has been investigated by *García-Cubero et al., 2009* and result showed that after hydrolysis up to 88.6 and 57 % fermentable sugar yields were obtained compared to 29 and 16 % in non-ozonated wheat and rye straw, respectively. In ozonolysis pretreatment process, Moisture content is the most significant factor. Effect of ozonolysis in combination with Wet Disk Milling (WDM) on Japanese cedar (*Cryptomeria japonica*) to improve sugar production was investigated by *Miura et al., 2012*. He reported that, when the moisture content increased more than 40 %, ozone consumption was decreased, which results less delignification. Another study, ozonolysis and WDM for pretreatment of sugarcane bagasse and straw was also investigated by *Barros et al., 2013*. After 60 min ozonolysis followed by WDM (4 cycles and 1.2 min/g), saccharification of sugar cane bagasse gives 89.7 % of glucose and 48.8 % of xylose whereas in case of straw, 92.4% of glucose and 52.3 % of xylose were obtained after WDM (4 cycles and 0.2 min/g) followed by 60 min ozonolysis. From the above study it is observed that type of biomass also an important factor for ozonolysis pretreatment process. Ozonolysis alone can be ineffective for removal of lignin though ozonolysis in combination with other pretreatment process such as WDM has shown promising results.

3.1.2.3. Physico-chemical pretreatment:

i. Steam explosion:

Steam explosion pretreatment process involves sudden reduction in pressure which makes an explosive decompression in lignocellulosic material. In this pretreatment process, effective removal of hemicellulosic sugar was occurred with increasing pretreatment temperature up to a

certain level (160-260°C). However, by further increase in temperature may decrease the total sugar recovery (*Josefsson et al., 2002; Sun et al., 2004; Varga et al., 2004*). Effects of steam explosion on sunflower stalks at 180–230 °C temperature has been investigated by *Ruiz et al., 2008*. Study showed that after pretreatment, highest hemicellulose recovery was obtained at 210 °C and maximum glucose yield was obtained at 220 °C in pretreated sunflower stalks. Another research work carried by *Negro et al., 2003* showed that steam explosion for poplar (*Populus nigra*) pretreatment at 210 °C and 4 min results 95% cellulose recovery. However, in order to avoid unnecessary degradation of the chemical and physical properties of the cellulose, correct selection of the steam explosion conditions are required. Severe pretreatment conditions may cause lower cellulose recovery from lignocelluloses after Steam explosion pretreatment process. To overcome this problem, *Eklund et al., 1995* studied steam pretreatment of willow with the addition of SO₂ or H₂SO₄ with the purpose of recover both cellulose and hemicellulose. It is reported that maximum 95% glucose yield was obtained when steam pretreatment was done with 1% SO₂ at 200 °C.

ii. Supercritical Fluid (SCF) Pretreatment:

In this physico-chemical pretreatment process, a supercritical fluid which possesses both liquid like density and gas-like diffusivity and viscosity is used for the breakdown of crystalline structure of different LB. SCF can penetrate into the crystalline structure of LB overcoming the mass transfer limitations associated with the other pretreatments process (*Gu et al., 2013*).

Supercritical carbon dioxide (CO₂) with a critical temperature (T_C) of 31°C and a critical pressure (P_C) of 7.4 MPa, normally used as an extraction solvent (*Schacht et al., 2008*) shows effective potential in biomass pretreatment. During the pretreatment process, CO₂ reacted with

water and formed carbonic acid which accelerated the hydrolysis process. Furthermore, explosive release of CO₂ also disrupts the crystalline structure of hemicellulose and cellulose, which increases the accessible surface area for hydrolysis (*Zheng et al., 1998; Luterbacher et al., 2010*). Effect of supercritical CO₂ pretreatment on a hardwood (Aspen) and softwood (southern yellow pine) with varying moisture contents (0-73% (w/w)) was investigated by *Kim et al., 2001*. Supercritical CO₂ treated biomass showed better sugar yields after the hydrolysis when compared to thermal pretreatments without supercritical CO₂. Furthermore, it was also reported that when moisture free biomass was used for pretreatment, the final reducing sugar yield from hydrolysis of this pretreated biomass was similar to that of untreated biomass. A comparison study between the effect of supercritical CO₂ alone and a combination of CO₂ and steam on dry and wet wheat straw under different operating condition was investigated by *Alinia et al., 2010*. It was found that maximum overall yield of sugars was achieved by applying the combination of supercritical CO₂ and steam pretreatment. Although, several research works have been done on SCF for pretreatment, implement of this process on a large scale has not proven to be economically feasible due to the high pressures involvement.

iii. Liquid hot-water (LHW) pretreatment:

Liquid hot-water pretreatment is an another hydrothermal pretreatment process much like steam explosion where water at higher temperature and pressure maintaining its liquid form was used for pretreatment of LB since several decades ago in pulp industries. The major benefits of LHW pretreatment over steam explosion are minor formation of inhibitory compounds and higher pentosan recovery (*Dien et al., 2006*). Water at high pressure can penetrate into the

crystalline structure of LB overcoming the mass transfer limitation and remove hemicellulose and part of lignin. Furthermore, in this process there is no requirement for extra chemical addition and corrosion-resistant ingredients for hydrolysis reactors.

An experiment using two-step liquid hot water pretreatment process for complete saccharification of *Eucalyptus grandis* was studied by *Yu et al., 2010*. At first step, total xylose yield was 86.4% at 180°C after 20 min and at second-step it is observed that minimal sugars degradation were occurred at 200 °C and 20 min. After enzymatic digestion of *Eucalyptus grandis* at the above optimized pretreatment conditions, total sugar yield was reached to 96.63%. *Laser et al., 2002* had performed a comparative study between the performance of LHW and steam pretreatments on sugarcane bagasse, which was successively used for production of ethanol by SSF. The pretreatment process was performed in a 25 l reactor at high temperature (170-230 °C) for 1-46 min with 1% to 8% solids concentration. The results showed that higher xylan recovery was achieved by LHW pretreatment compared to steam pretreatment. However, LHW pretreatment process consumes higher energy compared to steam pretreatment as it involves higher pressures and higher water supply to the system. LHW pretreatment were also beneficial over dilute-acid pretreatment processes, as there is no requirement for hazardous acids or production of neutralization wastes.

iv. *Ammonia fiber explosion (AFEX):*

Pretreatment of LB by ammonia fiber explosion (AFEX) process is considered to be an effective technique in which biomass is treated with liquid anhydrous ammonia at moderate temperatures (60°C-100°C) under high pressures (*Mosier et al., 2005; Kumar et al., 2009*). Similar to steam-explosion pretreatment process, the biomass is saturated with anhydrous

ammonia in a pressurized reactor for a period of time before being released to atmospheric temperature. At high pressure, ammonia causes swelling of LB which consequently disrupts the lignin structure and increases the surface accessibility for hydrolysis. Furthermore, it also promotes hemicellulose depolymerization and partial cellulose decrystallization (*Hendriks et al., 2009; Sousa et al., 2009*). *Alizadeh et al., 2005* investigated the effect of AFEX pretreatment on switchgrass. He reported that, the pretreatment process was optimized at a temperature of 100 °C, with an ammonia loading of 1 kg of ammonia per kilogram of dry matter, a moisture content of 80% (dry weight basis), and a residence time of 5 min. The hydrolysis of AFEX-treated samples results 93% glucan conversion whereas 16%, glucan conversion was achieved from untreated sample under the same hydrolysis condition. Besides, minimum formation of degradation products this pretreatment process has also some advantages which includes lower moisture content, nearly all ammonia recovery and its reusability.

3.1.2.4. Biological pretreatment:

Microorganisms such as brown, white and soft rot-fungi can also be used to degrade the lignocellulosic materials (*Zhang et al. 2007; Narayanaswamy et al. 2013*). These applied microorganisms have the ability to degrade hemicellulose and lignin part but leaves the cellulose intact, (*Sánchez et al., 2009; Nanda et al. 2014*). Biological pretreatment requires lower energy, mild operation conditions. (*Mousdale et al., 2008*). However, these pretreatments were not so efficient for biomass conversion owing to longer pretreatment times (several days) (*Cardona et al., 2007*).

3.2. Hydrolysis using homogeneous catalysts:

Previously homogeneous acid catalysts are employed for the acidic digestion of LB. For homogeneous catalyzed hydrolysis process, both inorganic acids (H_2SO_4 , HCl , and H_3PO_4) and organic acids (carboxylic acids, p-toluenesulfonic acid) can be used as catalyst. *Marzialetti et al., 2008* demonstrated utilization of different liquid acid catalysts for hydrolysis of Loblolly pine. A comprehensive study was also performed to investigate effect of pH, acid types, reaction temperature and reaction time on hydrolysis products using mineral acids viz. HCl , H_2SO_4 , HNO_3 , H_3PO_4 and Trifluoroacetic acid. Among these acids, Trifluoroacetic acid is found to be the promising one and results highest amount of overall soluble monosaccharides (~70% yield from the hemicelluloses fraction) at optimized temperature of 150°C and pH of 1.65. Similar to previous work, recently, *Hilpmann et al., 2016* reported that hemicellulose (xylan) can be selectively hydrolyzed by four different homogeneous acid catalysts (HCl , H_2SO_4 , trifluoroacetic acid, oxalic acid) at moderate temperature ($70\text{--}90^\circ\text{C}$) and experiment results higher xylose yields up to 95%. To get maximum sugars yield and minimize the formation of inhibitors optimization of acid hydrolysis parameters is important. In doing so, *Naseeruddin et al., 2016* conducted an experiment to optimized liquid acid catalyst concentration in biphasic dilute acid hydrolysis of delignified *Prosopis juliflora*. The experiment was performed using phosphoric acid, hydrochloric acid and sulfuric acid separately for biphasic acid hydrolysis of delignified *Prosopis juliflora* at 110°C for 10 min for phase-I and 121°C for 15 min for phase-II. He reported that, among three acids, sulfuric acid with concentration of 1 & 2% (v/v) in a biphasic combination, results maximum holocellulose (cellulose and hemicellulose) of $25.44 \pm 0.44\%$ releasing 0.51 ± 0.02 g/L of phenolics and 0.12 ± 0.002 g/L of furans respectively. Furthermore, reaction time and temperature for delignified substrate hydrolysis using the selected acid (H_2SO_4) was also

optimized by varying hydrolyzed $55.58 \pm 1.78\%$ of holocellulose releasing 2.11 ± 0.07 g/L and 1.37 ± 0.03 g/L of phenolics and furans, respectively at operating conditions of 110°C for 45 min in phase-I & 121°C for 60 min in phase-II. To avoid higher reaction temperature associated with dilute acid hydrolysis process, concentrated acids can be used for biomass hydrolysis (*Wijaya et al., 2014; Kumar et al., 2009*). *Lacerda et al., 2013* investigated the effect of concentrated sulfuric acid (25%) on mercerized sisal at moderate temperature (100°C). It was reported that sulfuric acid concentration at 25% favored glucose production up to 12% (approximately 10 g L^{-1}). The efficacy of concentrated acid catalysts was also investigated by (*Spronsen et al., 2011; Lacerda et al., 2015*). *Lacerda et al., 2015* also reported that oxalic acid at higher concentration (4.6 mol L^{-1}) for hydrolysis of sisal pulp results higher glucose concentration (8 g L^{-1}) at temperature of 100°C after 16h and the percentage of hydrolyzed cellulose under these conditions was 50.4%.

From literature review, it can be seen that mineral acids are effectively used at high temperature ($150\text{-}250^{\circ}\text{C}$) for hydrolysis process (*Iranmahboob et al., 2002; Orozco et al., 2011*) but there are also many problems associated with this hydrolysis process viz., equipment corrosion, acid separation from the product and environmental pollution. The drawbacks of previously published research activities on hydrolysis of LB with homogeneous catalysts are highlighted in **Table 3.2**.

Table 3.2: Drawbacks of previously published research activities on homogeneous hydrolysis of LB

Homogeneous Catalysts (w/w of Biomass)	Feedstock	Pretreatment Condition	Hydrolysis Conditions	Glucose Yield (%)	Drawbacks	Reference
H ₂ SO ₄ (0.02)	Corn cobs	–	403 K, 15min	3.2	Low product yield, High reaction temperature	<i>Rivas et al., 2008</i>
H ₂ SO ₄ (0.01)	Rye straw	Liquid hot water pretreatment	463K, 2h	43.6	High reaction time and temperature	<i>Rogalinski et al., 2008</i>
H ₂ SO ₄ (0.01)	Rye silage	Liquid hot water pretreatment	463K, 2h	39.9	High reaction time and temperature	<i>Rogalinski et al., 2008</i>
H ₂ SO ₄ (2.0)	oak wood	–	353K, 30min	34.53	High acid concentration	<i>Wijaya et al., 2014</i>
H ₂ SO ₄ (2.0)	pine wood	–	353K, 30min	29.94	Poor product yield and High acid concentration	<i>Wijaya et al., 2014</i>
H ₂ SO ₄ (2.0)	empty fruit bunch of	–	353K, 30min	31.68	Low product yield and	<i>Wijaya et al., 2014</i>

	palm oil				High acid concentration	
H ₃ PO ₄ (0.05)	municipal bio-waste, wood shavings	–	473K, 10min using Autoclave Parr reactor	30	Poor product yield, High reaction temperature	<i>Orozco et al., 2011</i>
H ₃ PO ₄ (0.3)	Potato peel	–	408K, 8min using Autoclave Parr reactor	46.02	Reaction temperature and pressure is high	<i>Lenihan et al., 2010</i>
H ₃ PO ₄ (0.5)	Yam (<i>Dioscorea sp.</i>)	Ultrasound irradiation	323K, 5h	20.5	Poor product yield and high reaction time	<i>Ramón et al., 2015</i>
HCl (0.025)	Bamboo	Cu ²⁺ ion, [C ₄ mim]Cl	373K, 4h	39.5	High reaction time	<i>Wang et al., 2014</i>

3.3. Hydrolysis using Heterogeneous Catalysts:

Reusable heterogeneous catalysts could be a probable option for hydrolysis of LB over enzymes or mineral acids. Uses of heterogeneous catalysts can overcome some of the drawbacks associated with the enzymes or mineral acids hydrolysis process and thus present a thought-provoking and possible opportunity to be used as effective catalyst in biomass hydrolysis

process. In last few decades, utilization of solid acid catalysts as heterogeneous catalyst for hydrolysis process has been coming up to a promising methodology. Up to now, several solid acid catalysts such as carbonaceous acids, H-form zeolites, heteropoly acids, functionalized silicas, metal oxides, supported metals and acid resins are used into the cellulose hydrolysis process. This type of catalysts carry $-\text{SO}_3\text{H}$, $-\text{COOH}$, and $-\text{OH}$ functional groups that results higher catalytic activity over conventional acid catalysts. This lies in the fact that their potentiality to adsorb β -1,4glucan resulting good access of reactants to the acidic sites of $-\text{SO}_3\text{H}$ groups (*Guo et al., 2012; Bootsma et al., 2007*).

To understand the efficacy of carbon based catalyst, *Suganuma et al., 2010; Suganuma et al., 2011* had compare carbon based catalyst against homogeneous H_2SO_4 catalyst. Literature reported 10% glucose yield using H_2SO_4 (20.4mmol g^{-1}) for hydrolysis of crystalline cellulose. The same research group developed carbon material based catalyst possessing $-\text{SO}_3\text{H}$ group (1.9mmol g^{-1}) rendering 4% glucose yield. Remarkably, for fermentable sugar production, carbon based sulfonated catalyst enumerated lower activation energy compared to conventional H_2SO_4 . The efficacy of carbon based catalyst also investigated by *Sakdaronnarong et al., 2016* and *Zhong et al., 2015*. *Zhong et al., 2015* also reported that hemicellulose can be selectively hydrolyzed by nanoscale solid catalysts. Thus, carbon based solid catalyst serve as a good replacement for conventional and corrosive homogeneous H_2SO_4 catalyst. The catalyst revealed excellent acid density and superior stability in terms of catalytic activity and reusability (**Figure 3.3**).

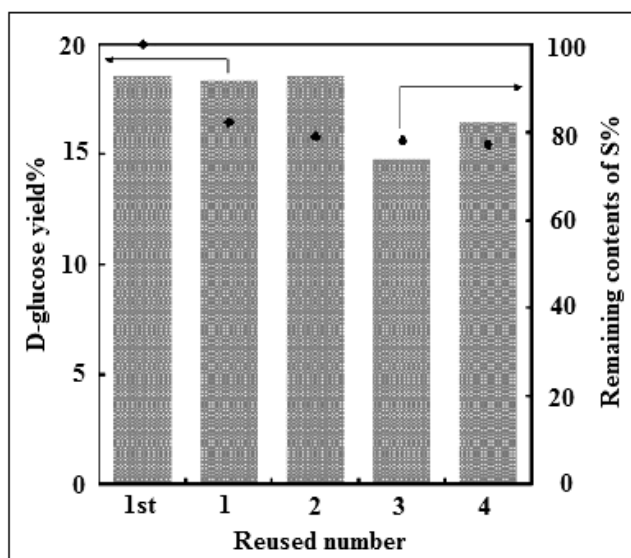


Figure 3.3: Catalytic activity of reused carbon-based solid acid for hydrolysis of cellobiose and the remaining S content in the catalyst after reactions (*Suganuma et al., 2010*).

Amberlyst-15 is a cation exchange resin which is used commercially for effective conversion of cellulose in hydrolysis process. Its structure acts like a membrane which allows penetration of reactants to the site of hydrogen ions during the hydrolysis reaction. Furthermore, inhibitors which are produced after hydrolysis process can also be removed by this type of catalyst which is an advantage over the other types of carbon based catalysts. *Onda et al., 2008* reported that hydrolysis of 45mg cellulose in 5mL distilled water for a time span of 24h by 50mg of Amberlyst-15 resulted more than 25% yield of glucose at 150 °C. Similar to the above study, *Meena et al., 2015* also performed an experiment using amberlyst-15 for hydrolysis of pretreated rice straw. The result showed that maximum 255mg/g sugar yield was achieved after 4h hydrolysis at 7% biomass and catalyst loading.

Although solid carbon catalysts have large surface area, strong acidity, they have been difficult to use effectively in large scale due to mass transfer limitations, high catalysts costs, and high energy consumption. The drawbacks of previously published research activities on hydrolysis of LB with homogeneous catalysts are highlighted in **Table 3.3**.

Table 3.3: Drawbacks of previously published research activities on heterogeneous hydrolysis of LB

Heterogeneous Catalysts (mg/mg of biomass)	Feedstock	Pretreatment Method	Hydrolysis Condition	Glucose Yield (%)	Drawbacks	Reference
Amberlyst-15 (1.11)	Cellulose	Milling	423K, 24h	25	Poor glucose yield, high reaction temperature and time	<i>Onda et al., 2008</i>
AC-SO ₃ H (1.11)	Microcrystalline Cellulose	Milling	423K, 24h	40	high reaction temperature and time	<i>Onda et al., 2008</i>
H-ZSM5 (1.11)	Microcrystalline Cellulose	Milling	423K, 24h	12	Low glucose yield, reaction time and temperature is	<i>Rinaldi et al., 2008</i>

					high	
Amberlyst-15 (1.0)	Cellulose	----	423K, 3h	15	Poor glucose yield and high reaction temperature	<i>Lai et al., 2011</i>
Fe ₃ O ₄ -SBA-SO ₃ H (1.5)	Corn cob	----	423K, 3h	45	Reaction temperature and time is high	<i>Lai et al., 2011</i>
Fe ₃ O ₄ -SBA-SO ₃ H (1.5)	Microcrystalline Cellulose	[BMIM]Cl	423K, 3h	50	Reaction temperature and time is high	<i>Lai et al., 2011</i>
Dowex 50wx8-100 ion-exchange resin (0.52)	Microcrystalline Cellulose	[EMIm]Cl	383K, 4h	83	Reaction time is high	<i>Qi et al., 2011</i>
Amberlyst-15 (1.0)	Rice Straw	Alkali Pretreatment	408K, 4h	25.5	Low product yield, temperature is high	<i>Meena et al., 2015</i>
Glycerol based	Rice Straw	Alkali	413K, 4h	26.2	Low product	<i>Gosw</i>

Carbon Acid Catalyst (1.0)		Pretreatment			yield, temperature is high	<i>ami et al., 2015</i>
CMC-SO ₃ H (0.6)	Microcrystalline Cellulose	[BMIM]Cl	403K, 4h	78.5	Reaction temperature and time is high	<i>Hu et al., 2016</i>
CMC-SO ₃ H (0.6)	Rice Straw derived cellulose	[BMIM]Cl	403K, 4h	73.2	Reaction temperature and time is high	<i>Hu et al., 2016</i>

[AC-SO₃H: Sulfonated activated-carbon; H-ZSM5: Zeolite Socony Mobil-5; Fe₃O₄-SBA-SO₃H: Sulfonic group functionalized magnetic SBA-15 catalyst; CMC-SO₃H: cellulose mimetic catalyst]

3.4. Intensification Techniques:

Recently, some Intensification techniques viz. microwave, ultrasound, infrared radiation (IR) are used for effective hydrolysis of the biomass and enhance the conversion yield. Several research works have been investigated to understand the efficacy of these auxiliary techniques in hydrolysis process, which are discussed in more detail in the following sections.

i. Microwave Irradiation:

In last few years, microwave heating has been adopted in biomass hydrolysis process to accelerate the hydrolysis rate and reduce the reaction time as compared with conventional

heating mode. The rapid rise in temperature due to microwave heating causes intra-water vaporization in biomass which consequently increases intra-particle pressure to untie the biomass structure and thus reduced the cellulose crystallinity (*Xue et al., 2011; Chen et al., 2011*). The absorption capacity of microwave energy (600-1600 W) is different for different lignocellulosic components (*Wan et al., 2009*). *Wu et al., 2010* performed an experiment with biomass char sulfonic acid catalyst for hydrolysis of crystalline cellulose in water under microwave heating. He reported that using microwave heating at 90°C for 60 min can result up to 24.1% of reducing sugar yield which was 3.8 times higher than that for conventional heating. The uses of microwave heating with ionic liquids to enhance the hydrolysis process were also focused as they have good solubility for cellulose. *Zhang et al., 2009* reported that within 8 min up to 37% reducing sugar yield can be achieved by hydrolyzing Avicel cellulose in ionic liquid 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) under microwave heating (80 W). He also reported that, higher MI power (400 W) can cause degradation of glucose and produce some byproducts such as 5-hydroxymethyl furfural, humins.

ii. *Ultrasonic Treatment:*

Ultrasonic treatment is another process intensification technique for biomass hydrolysis where ultrasonic energy is used to depolymerize the biomass structure by using an ultrasonic probe or an ultrasonic bath. The ultrasound assisted pretreatment destroys intermolecular hydrogen bonds between lignocellulosic components and enhances lignocellulose dissolution (*Tang et al., 2005; Werle et al., 2015*). Furthermore, it also endorses solvent penetration into cellulosic materials and thus increases mass transfer rate. *Velmurugan et al., 2011* investigated the effect of ultrasound pretreatment on sugarcane bagasse with 10% NaOH for 1 h in an autoclave. The results showed that after pretreatment, 95% lignin reduction is occurred whereas

79% cellulose and 99% hemicellulose recovery was achieved. Ultrasonic treatment also altered the cellulose structure and improves the cellulose accessibility to catalysts (*Mikkola et al., 2007; Lan et al., 2011*). *Lan et al., 2011* reported that by assistance of 30W ultrasound energy for 20 min can reduce the complete dissolution time of cellulose in 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) from 190 min to 60 min.

CHAPTER-4

AIMS AND OBJECTIVES

4. Aims and Objectives:

The key objectives of the present research are as follows:

- I. Identification of appropriate process factors viz. reaction temperature, catalyst concentration, batch time, water loading, NH₄OH loading.
- II. Optimization of process factors for hydrolysis reaction to maximize the desired product yield.
- III. Reduction of hydrolysis reaction time and reaction temperature; hence, minimization of energy consumption and the overall operating cost.
- IV. Intensification of the one-pot hydrolysis of WPP.
- V. Analyses of the raw WPP and hydrolysis product by XRD (X-ray diffraction), FTIR (Fourier transform infrared spectroscopy), and HPLC (High performance liquid chromatography).

CHAPTER-5

MATERIALS AND METHOD

5. Materials and Method:

5.1. Materials:

The waste papaya peels (WPP) were collected from the local fruit shops and all the chemicals used were of analytical reagent grade. Aqueous NH_4OH (25%), Acetone, DNS (di-nitro salicylic acid) etc. were purchased from Merck (India), Amberlyst-15 (with a macro reticular matrix with an average particle size of 0.35-1.2 mm) was purchased from Sigma Aldrich.

5.2. Reactor configurations and reaction procedure:

The AFEX pretreatment (*Balset et al., 2011; Zhong et al., 2009; Balan et al., 2009*) of WPP was carried out in a three-neck flask using a far infrared radiated reactor (FIRRR) (150 W; far infrared wavelength: 2700–30,000 nm). A mechanical stirrer with speed controller was fitted at the central neck of the flask and uniform temperature (isothermal) was maintained by using a PID temperature controller. In one-pot conversion in the FIRRR, for pre-treatment purpose, a measured quantity of WPP was taken into the three-neck flask, followed by addition of measured quantity of deionized water and aqueous NH_4OH and the mix was stirred at 400 rpm at a controlled temperature for the specified duration (as per **Table 5.6 (a)**). After pretreatment, the reactor content was water-washed to remove the excess NH_3 . Subsequently for hydrolysis, measured quantity of water and amberlyst-15 catalyst were added to the reactor content and stirred at 400 rpm at a controlled temperature for a specified time (**Table 5.6 (a)**). Afterwards, the catalyst and residue PWPP were separated through vacuum filtration of reaction mix and the filtrate was used for determination of glucose concentration by standard DNS method *Miller et al., 1959*.

5.3. X-ray diffraction analysis (XRD):

The changes in crystalline structural of the cellulose for raw WPP, optimally pre-treated WPP and optimally hydrolyzed PWPP residue samples were investigated by the XRD analysis using an X-ray diffractometer (INTEL CPS 120 hemispherical detector, Rigakuminiflex Co. Japan) at 40 kV and 30 mA. The diffracted intensity of Cu K α radiation was measured at 1.5418 Å wavelengths in a 2θ range between 0° and 50°.

5.4. Fourier transform infrared spectroscopy (FTIR):

FTIR analyses (FTIR-Shimadzu Alpha, from 400cm⁻¹ to 4000cm⁻¹) of raw WPP, optimally pre-treated WPP and optimally hydrolyzed PWPP residue samples as well as of product liquor were analyzed to detect the chemical characteristic of the samples.

5.5. High performance liquid chromatography (HPLC):

The hydrolysis product was further analyzed through an Agilent 1200 series HPLC unit provided with a refractive index detector (RI-HPLC) and a Biorad HPX-87H column, eluted by deionized water at a flow rate of 0.6 mLmin⁻¹. The concentration of each compound in hydrolysis product was determined through calibration curves prepared by analyzing standard solutions of respective compounds of known concentrations.

5.6. Optimization:

The TOD['MINITAB-16': Minitab Inc. USA for Windows7] provides a set of 9 numbers of experiments(L₉)to evaluate the impact of all process parameters on the response variable and a set of optimal process parameters corresponding to maximum Ω gthrough estimation of signal to noise(S/N) ratios and analysis of variance (ANOVA) *Tosun et al., 2004*. Here, signal (S) represents the arithmetic mean of three experimental replication values of the

response (Ωg) whereas the noise (N) is the standard deviation. The S/N ratios are calculated using the glucose yield (Y_i) of each trial as presented by Eq. (1):

$$S / N = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (1)$$

Where, i denotes the number of repetitions; n is the number of experiments performed in any particular parametric combinations as per **Table 5.6 (b)**.

In pretreatment process, the four independent parameters chosen for the process design were reactor temperature (Θ_T), batch time (Θ_t), NH_4OH loading (Θ_{np}) and water to PWPP weight ratio (Θ_{wp}) while Ωg was selected as the dependent parameter (response variable) (**Table 5.6 (a)**). The optimal parameters for pretreatment were evaluated. Afterwards, the hydrolysis process was performed by selecting reactor temperature (Θ_T), batch time (Θ_t), catalyst concentration (Θ_{pc}) and water to PWPP weight ratio (Θ_{wp}) as independent parameters (Table 1) with an objective to maximize the Ωg . In both pretreatment and hydrolysis, the response parameter (Ωg) has been optimized using the 'higher is better' algorithm for S/N ratio.

Table 5.6 (a): Independent experimental parameters and levels for pretreatment-hydrolysis system of WPP

Process parameters	Pre-treatment				Hydrolysis			
	Θ_T (°C)	Θ_t (min)	Θ_{np} (w/w)	Θ_{wp} (w/w)	Θ_T (°C)	Θ_t (min)	Θ_{pc} (wt.%)	Θ_{wp} (w/w)
L1	50	10	0.5	5	60	10	2.5	10
L2	70	20	1.5	10	70	15	5	20
L3	90	30	2.5	15	80	20	7.5	30

Table 5.6 (b): Taguchi orthogonal design for pretreatment-hydrolysis system of WPP

Trial no	Pre-treatment							Hydrolysis		
					Ω_g	Std	S/N ratio	Ω_g	Std	S/N ratio
1	L1	L1	L1	L1	18.36	$\pm.014$	25.28	36.36	$\pm.260$	31.21
2	L1	L2	L2	L2	19.71	$\pm.021$	25.8	39.09	$\pm.032$	31.84
3	L1	L3	L3	L3	21.49	$\pm.150$	26.65	43.24	$\pm.230$	32.72
4	L2	L1	L2	L3	23.23	$\pm.022$	27.32	70.38	$\pm.017$	36.95
5	L2	L2	L3	L1	36.42	$\pm.017$	31.46	87.16	$\pm.110$	38.81
6	L2	L3	L1	L2	27.54	$\pm.120$	28.79	40.79	$\pm.028$	32.21
7	L3	L1	L3	L2	29.28	$\pm.039$	29.33	88.21	$\pm.015$	38.91
8	L3	L2	L1	L3	25.80	$\pm.110$	28.23	55.69	$\pm.140$	34.92
9	L3	L3	L2	L1	35.76	$\pm.016$	31.07	59.59	$\pm.022$	35.50

L1=Low level value, L2=Middle level value, L3=Upper level value.

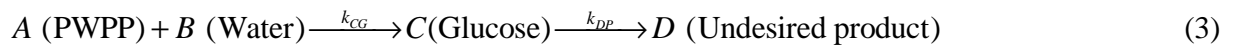
5.7. Development of reaction kinetic models:

In the present study a modified PHPF hydrolysis reaction model has been formulated to determine the kinetic parameter of the hydrolysis of PWPP at TOD predicted optimal process conditions.

5.7.1. PHPF first order reaction formalism

Formulation of pseudo-homogeneous pseudo-first order reaction kinetic models of PWPP under optimal process conditions are based on conventional assumptions; viz. hydrolysis rate is independent of excess water concentration (*Chong et al., 2004; Jeonget al., 2012*) (pseudo-first order approximation); the PWPP hydrolysis is a consecutive irreversible first order series reactions (*Saemens,1945; Rafiqulaet al., 2012*).

The conventional PH model has been modified through a rational consideration of initial glucose concentration of PWPP; i.e. $C_{C_0} \neq 0$ (2)



$$r_C = \frac{dC_C}{dt} = k_{CG} C_A C_B - k_{DP} C_C \quad (4)$$

Where k_{CG} and k_{DP} are the reaction rate constants for formation of glucose and deformation of glucose respectively.

$$\text{After integration from } t=0, C_C = C_{C_0} \text{ to } t=t, C_C = C_C \quad (5)$$

This Eq. (4) can be rewritten as follows:

$$C_C = C_{C_0} + k_{CG} C_A C_B t - k_{DP} C_C t \quad (6)$$

The reaction rate constant k_{CG} follows Arrhenius equation:

$$k_{CG} = E_{CG} \exp \left[-\frac{E_{CG0}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

Where E_{CG} = the activation energy (kJ/mol) and E_{CG0} = pre-exponential factor; $R=8.314 \times 10^{-3}$ (kJ/mol.K).

The kinetic rate constant(k_{CG}) was evaluated using build-in nonlinear applying MATLAB R2013b.

CHAPTER-6

RESULT AND DISCUSSION

6. Result and Discussion:

6.1. Individual parametric effects and optimal conditions for pretreatment process:

Analysis of variance of the process parameters which affect the WPP pretreatment process in the FIRRR is presented in **Table 6.1 (a)**.

Table 6.1 (a) indicates that, the reaction temperature and water to WPP ratio are statistically significant process parameters at 95% confidence level (p -value < 0.05). Notably, the process parameter corresponding to higher Δ -value exhibited (**Table 6.1 (b)**) greater effect on the response parameter (Ωg) compared to the other process parameters. From **Table 6.1 (b)**, it can be concluded that relative significance of the process parameters on the response parameter (Φ_{RS}) were $\Theta_T > \Theta_{wp} > \Theta_{np} > \Theta_t$. Moreover it was also observed that (**Table 6.1 (b)**), the reaction temperature and catalyst to PWPP ratio are statistically significant process parameters at 95% confidence level (p -value < 0.05). Notably, the process parameter corresponding to higher Δ -value exhibited (**Table 6.1 (b)**) greater effect on the response parameter (Ωg) compared to the other process parameters. From Table 3, it can be concluded that relative significance of the process parameters on the response parameter (Ωg) were $\Theta_T > \Theta_{pc} > \Theta_t > \Theta_{wp}$.

Table 6.1 (a): Analysis of variance (ANOVA) of factors affecting WPP pretreatment and subsequent hydrolysis process

WPP pretreatment					PWPP hydrolysis						
Source	D	Sum of square	Adjusted mean square	F value	p-value	Source	D	Sum of square	Adjusted mean square	F value	P value
$\Theta_T(^{\circ}C)$	1	162.99	162.99	13.60	0.021	$\Theta_T(^{\circ}C)$	1	1198.47	1198.47	13.02	0.023

$\Theta_t(\text{min})$	1	32.27	32.27	2.69	0.17	$\Theta_t(\text{min})$	1	439.35	439.35	4.77	0.09
					6						4
$\Theta_{np}(\text{w/w})$	1	45.19	45.19	3.77	0.12	Θ_{pc}	1	1225.6			
)					4	(wt.%)	1	1225.67	13.3	0.02	
									1	2	
$\Theta_{wp}(\text{w/w})$	1	73.43	73.43	6.13	0.04	$\Theta_{wp}(\text{w/w})$	1	31.74	31.74	0.34	0.58
)					9)					9
Error	4	47.92	11.98			Error	4	368.27	92.07		
Total	8	361.8				Total	8	3263.5			
		0						0			

Table 6.1 (b): *S/N* ratios at different levels of process parameters and Δ -values in pretreatment and subsequent hydrolysis process

Level	WPP pretreatment				PWPP hydrolysis			
	Θ_T	Θ_t	Θ_{np}	Θ_{wp}	Θ_T	Θ_t	Θ_{pc}	Θ_{wp}
1	25.94	27.31	27.44	29.27*	31.92	35.69*	32.78	35.17*
2	29.19	28.53	28.09	28.01	35.99	35.19	34.76	34.32
3	29.54*	28.84*	29.14*	27.40	36.44*	33.22	36.33*	34.86
Delta (Δ)	3.60	1.53	1.71	1.87	4.52	2.21	4.03	0.85
Rank	1	4	3	2	1	3	2	4

The maximum *S/N* ratio values corresponding to the process parameters are marked using asterisk (**Table 6.1 (b)**) indicating that maximum Ω in pretreatment could be achieved at 90°C Θ_T , 5 Θ_{wp} , 30 min Θ_t , and 2.5 Θ_{np} . Also the maximum *S/N* ratio values corresponding to

the process parameters are marked using asterisk (**Table 6.1 (b)**) indicating that maximum Ω_g (88.21%) in hydrolysis could be achieved at 80°C θ_T , $7.5\theta_{pc}$, 10 min θ_t , and 10 θ_{wp} .

6.2. Interaction among process parameters for pretreatment-hydrolysis process:

Keeping other factors at optimal, an increment in pretreatment temperature for any given time (θ_t) resulted higher Ω_g and vice-versa (**Figure 6.2 (b) a**). These indicate that, the medium was thermally sensitive. Similarly gradual increase in temperature resulted in higher Ω_g and vice-versa at all values of θ_{np} (**Figure 6.2 (b) b**). On the other hand from **Figure 6.2 (b) b** it could be concluded that, θ_{wp} has negative influence on Ω_g over the temperature range of pretreatment. From **Figure 6.2 (b) d**, it is observed that, at higher $\theta_{np} \geq 2.3$, Ω_g increased with time due to the greater accessibility of NH_4OH to cellulose. For a specific pretreatment time, increasing θ_{wp} resulted lower Ω_g (**Figure 6.2 (b) e**). A similar trend was followed in **Figure 6.2 (b) f**, which again depicted negative effect of increasing θ_{wp} on Ω_g for all values θ_{np} considering the present study.

In one-pot process, after pretreatment, in consecutive hydrolysis step, keeping other parameters at optimal level, an increase in temperature could enhance Ω_g up to about 12.5 min. beyond that time, possibility of glucose decomposition could occur (**Figure 6.2 (b) g**). A gradual increase in hydrolysis temperature could accelerate glucose yield at higher catalyst concentration ($\theta_{cp} \geq 4.9$) (**Figure 6.2 (b) h**). From **Figure 6.2 (b) i**, it can be concluded that, the augmented yield of glucose could be attained at higher temperature independent of θ_{wp} values.

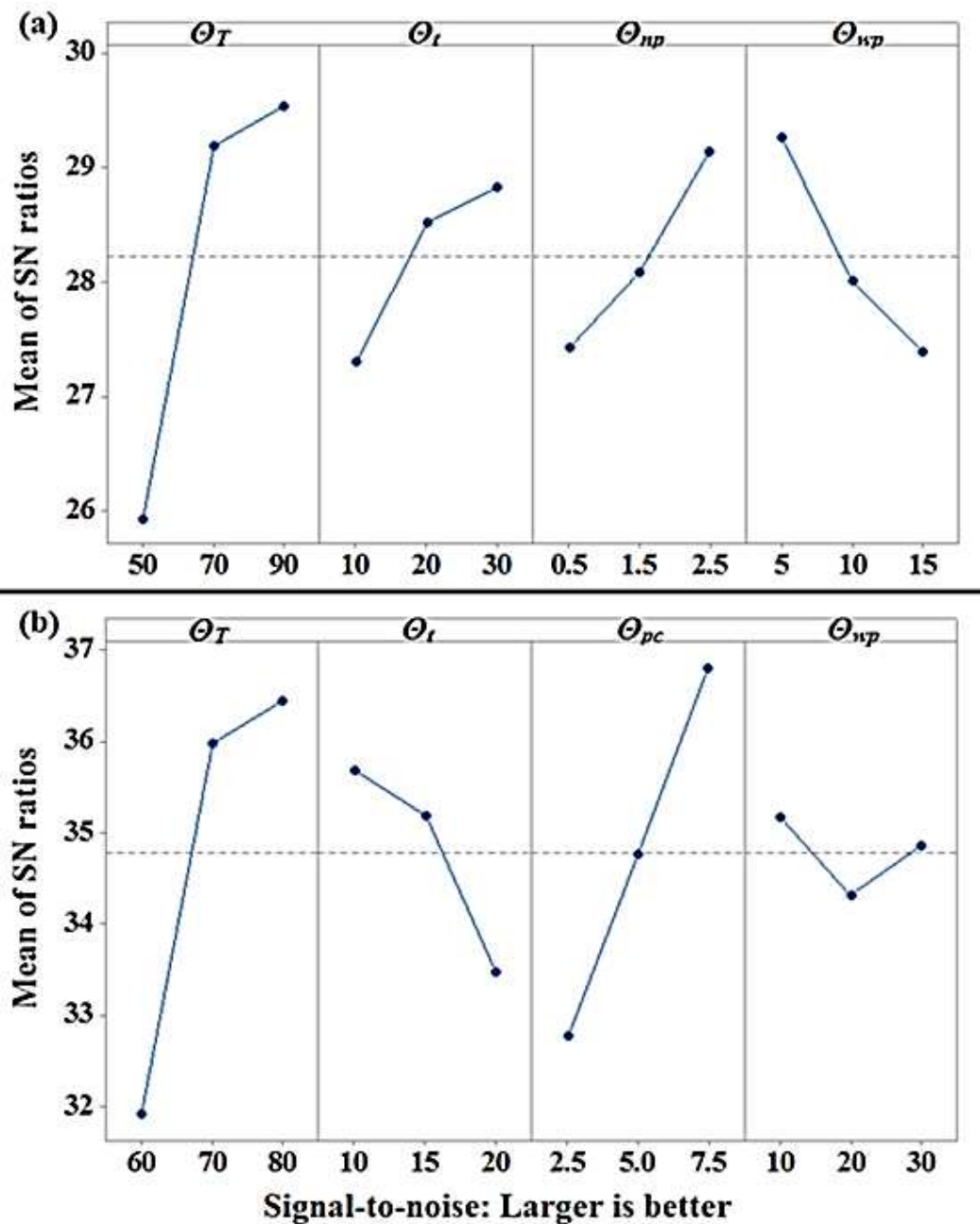


Figure 6.2 (a): Individual parametric effect for each process parameter for (a) Pretreatment; (b) Hydrolysis process obtained in FIRRR at optimal condition.

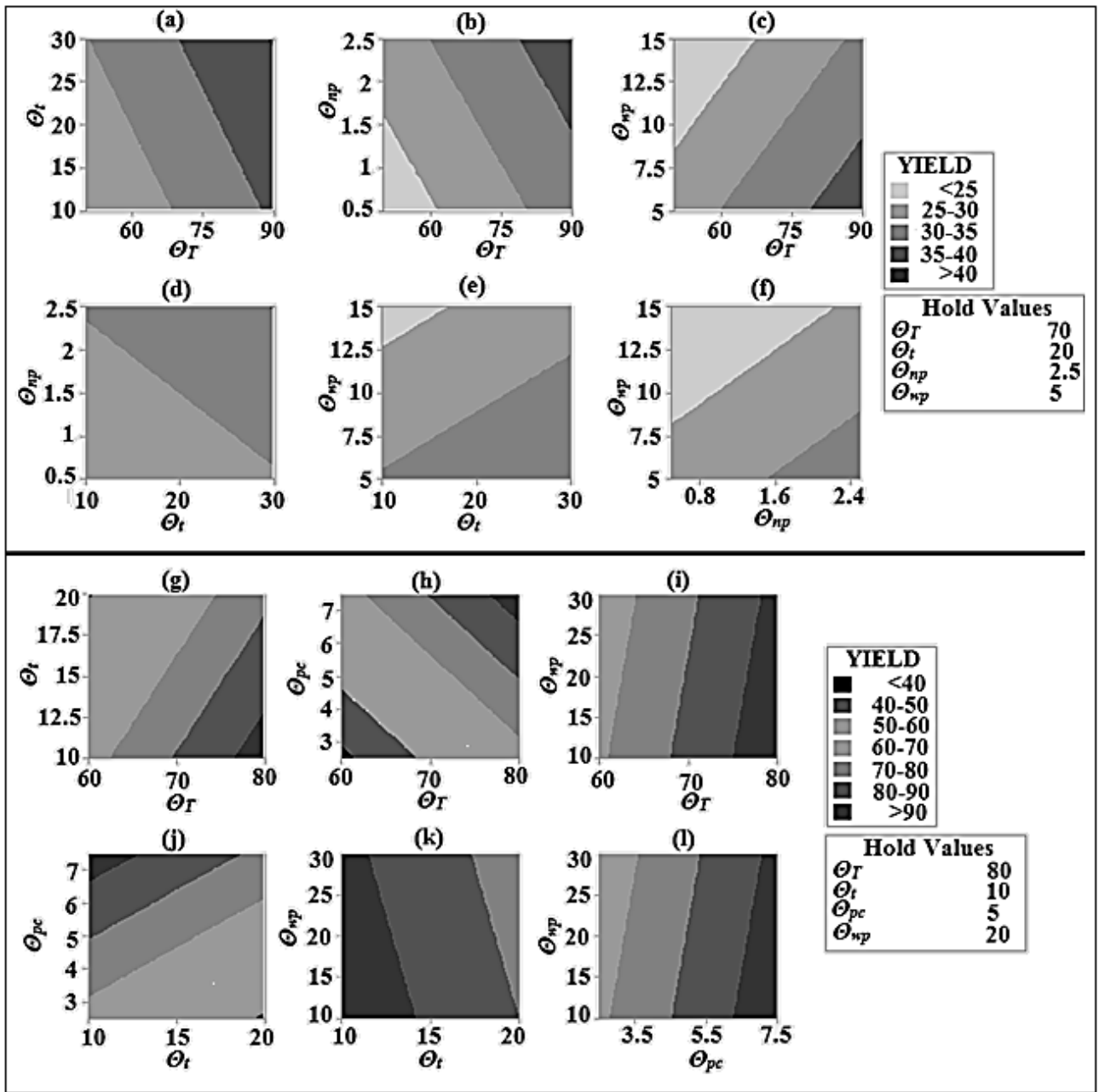


Figure 6.2 (b): Interaction plot for glucose yield for Pretreatment ((a)-(f)) and hydrolysis ((g)-(l)) of WPP

Moreover it is observed from **Figure 6.2 (b) j** that, at high $\theta_{cp} \geq 5.0$, Ω_g increased. But as time spend, Ω_g gradually decreased. An increment in hydrolysis time for any given θ_{wp} resulted lower Ω_g and vice-versa (**Figure 6.2 (b) k**). On the other hand, From **Figure 6.2 (b) gl**, it can be concluded that, the increased yield of glucose could be achieved at higher catalyst concentration (θ_{cp}) independent of θ_{wp} values.

6.3. Verification Test:

In order to validate the TOD predicted optimal process parameters for both pretreatment and hydrolysis process, pretreatment of WPP and hydrolysis of PWPP were conducted at the derived optimal parametric values (**Table 6.1 (b)**). The result indicated an acceptable standard deviation of Ω_g (mol %) of ± 0.227 to ± 1.243 and ± 0.198 to ± 1.517 respectively for pretreatment and hydrolysis process using FIRRR. Under identical optimal process conditions, the Ω_g in one pot pretreatment-hydrolysis process in CHSBR resulted in 36.42 mol% and 88.21 mol% in pretreatment and subsequent hydrolysis respectively.

6.4. Effect of Infrared radiation on hydrolysis kinetics at optimal condition:

Figure 6.4 depicts the glucose concentration variation with time at optimal hydrolysis condition in one-pot FIRRR. It can be observed that the glucose concentration increased with increase in hydrolysis time up to 10 minutes under FIR radiation and attains a maximum value of 0.111 mol /L corresponding to Ω_g of 88.21mol%. On the contrary, in case of CHSBR the glucose concentration increases slowly due to low reaction rate and achieves a maximum value of 0.0499 mol /L corresponding to Ω_g of 36.42 mol% within same period of hydrolysis time (10 min).

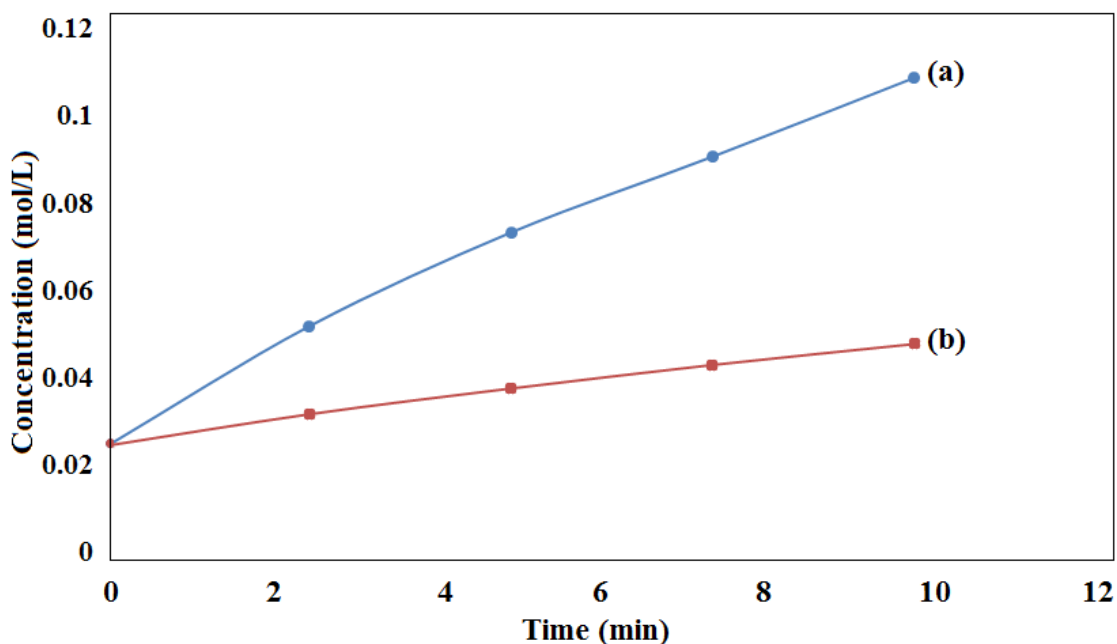


Figure 6.4: Variation of glucose concentration with time at optimal condition in hydrolysis of PWPP obtained in (a) FIRRR; (b) CHSBR

The main aim of the present work was to assess the effect of FIR radiation in the hydrolysis reaction along with the pretreatment process in intensifying conversion of PWPP to glucose in a one-pot pretreatment-hydrolysis system. In the present process, it is found that FIR radiation (150 W) could applicably accelerate the hydrolysis conversion significantly; thus, shortening the pretreatment-hydrolysis time to achieve the highest Ω_{gin} in comparison with the conventional heating protocol (500 W). The conversion of WPP to glucose could be enormously augmented and intensified significantly as FIR radiation (*Chakraborty et al., 2015*) could penetrate pretreatment-hydrolysis reaction mix deeper and get absorbed intensely into different cellulosic-layers to breakdown the crystalline structures. Besides, the interactions between the FIR radiation and the reactant molecules enhance stretching vibration rendering severe molecular collisions, thus, facilitating both pretreatment of WPP and hydrolysis of PWPP. Hence, the

conversion of WPP to glucose employing FIR radiation can be considered as an energy-efficient, time saving and cost-effective method for synthesis of glucose.

6.5. Kinetics of PWPP hydrolysis at optimal condition:

The hydrolysis kinetic model at the Taguchi derived optimal condition has been evaluated using the modified PH model Eq. (4) employing MATLAB R2013b. The goodness of fit along with other model fit parameters is presented in **Table 6.5**.

The reaction rate constant and activation energy for PH models for FIRRR at several temperatures have been presented in **Table 6.5**.

Table 6.5: Hydrolysis kinetic parameters and activation energy computed from different models for FIRRR.

	Apparent reaction rate constants	Temperatures			kinetic Parameters		Statistical Parameters		
		333 k	343 k	353 k	$E_{CG}(\text{kJ/mol})$	E_{CG0}	R^2_{adj}	RMSE	Model p-value
PH(FIRRR)	k_{CG}	0.00104	0.00132	0.00153	18.84	0.95	0.959	0.000638	6.32e-08
PH(CHSBR)	k_{CG}	0.000295	0.000389	0.00044	19.57	0.355	0.974	9.13e-05	5.09e-08

From **Table 6.5**, it is quite evident that the reaction rate constants are much greater at all temperatures under FIRRR in comparison with CHSBR. Besides, the activation energy computed under optimal process conditions indicate much lower values in case of FIRRR compared to CHSBR, signifying lower energy requirement while achieving significantly greater and faster glucose yield by employing FIRRR.

6.6. FTIR analyses of hydrolysis product:

Optimal hydrolysis products were analyzed through FTIR spectroscopy using FIRR (Fig. 11a) and using CHSBR (Fig. 11b). The vibration at 3426.51 cm^{-1} could be ascribed to the presence of O-H group. The stretching vibration at 1410.28 cm^{-1} corroborated the existence of H-C-H group (Socrates *et al.*, 2004). These spectra confirm the characteristic functional groups of sugars. The sharp peaks at 1689.43 cm^{-1} , 1150.14 cm^{-1} could be assigned to C=C and C-O-C bonds respectively (Socrates *et al.*, 2004).

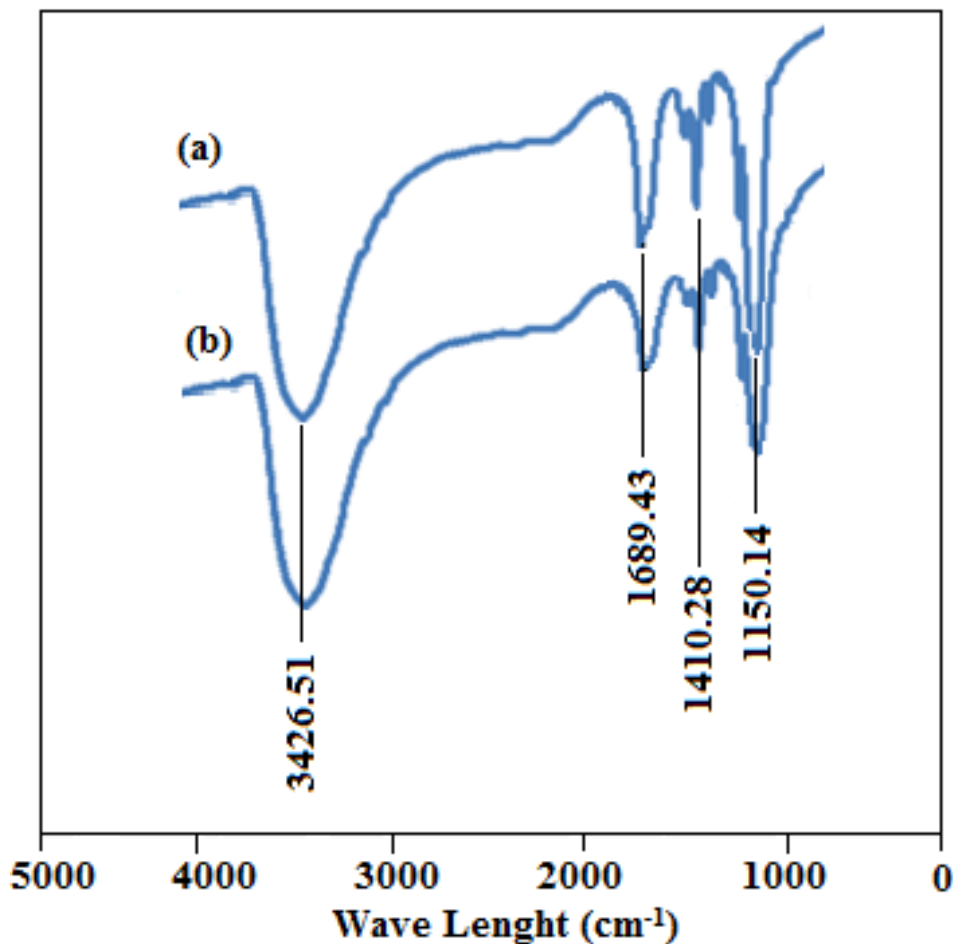


Figure 6.6: FTIR analyses of hydrolysis product derived from WPPP at optimal condition (a) FIRR; (b) CHSBR.

6.7. XRD Analysis of WPP:

The X-ray diffractogram of raw WPP (**Fig. 12a**), optimally pre-treated WPP (**Fig. 12b**) and optimally hydrolyzed PWPP residue by employment of FIRRR (**Fig. 12c**), demonstrated appreciable peak at $2\theta=21.8^\circ$ ascribing to crystalline phase of cellulose (*Wang et al., 2006*). It may be apprehended that the cellulose peak intensity became sharper due to the effect of pretreatment and subsequent hydrolysis process (*Zhao et al., 2007*).

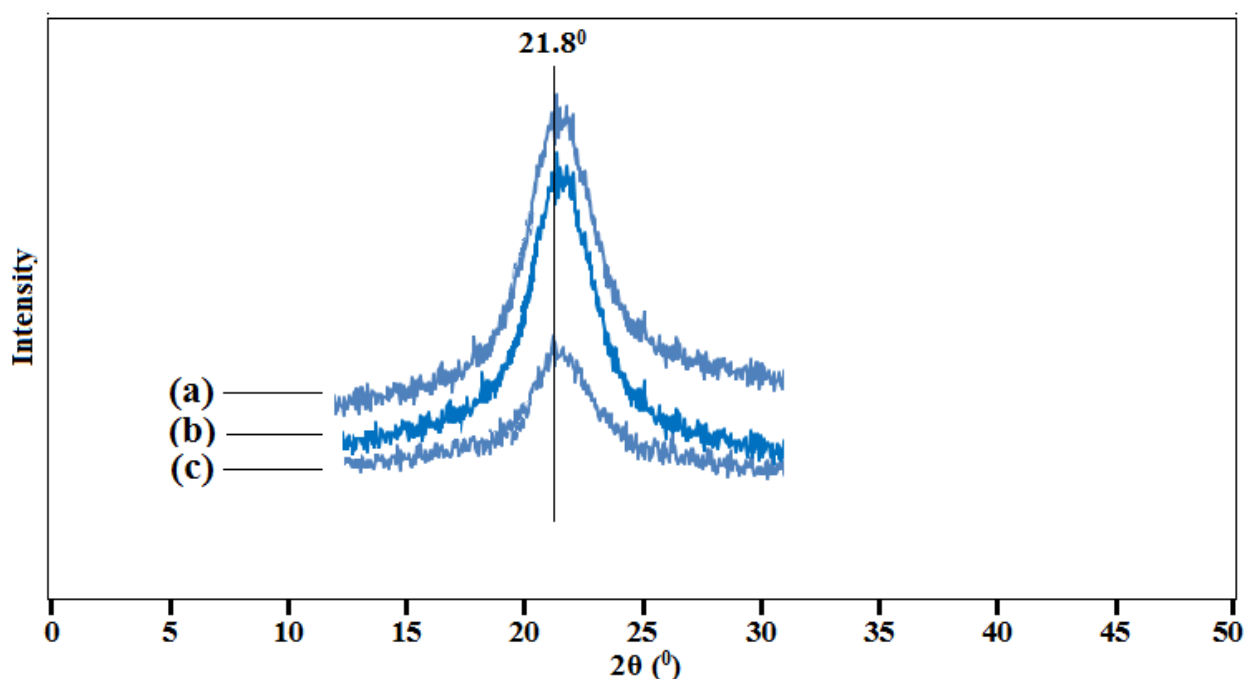


Figure 6.7:XRD analyses using FIRRR of (a) PWPP residue after hydrolysis; (b) WPP after pretreatment; (c) raw WPP at optimal condition.

6.8. FTIR analyses of WPP:

The characteristic functional groups in raw WPP (**Fig. 13a**), optimally pre-treated WPP (**Fig. 13b**) and optimally hydrolyzed PWPP residue (using the FIRRR) (**Fig. 13c**) were determined by FTIR spectra. The stretching vibration at 3302.13 cm^{-1} represents O-H functional

group while the existence of H-C-H bands were detected at 1413.82 cm^{-1} (Satyamurthy *et al.*, 2011). A significant peak at 1612.49 cm^{-1} indicates the presence of the O-H vibration of adsorbed water molecules. The peak located at 1026.13 cm^{-1} was attributed to the existence of C=O vibrations. Moreover, the CH₂ asymmetric stretching was recorded at 2918.29 cm^{-1} (Oh *et al.*, 2005). Additionally, CH deformation stretching peak was detected around 1321.24 cm^{-1} . It can be evidenced from Fig. 13a to Fig. 13c that, gradual augmentation in peak areas occurred corresponding to transformation from raw WPP to pre-treated WPP and finally to hydrolyzed WPP (Meyabadiet *al.*, 2014).

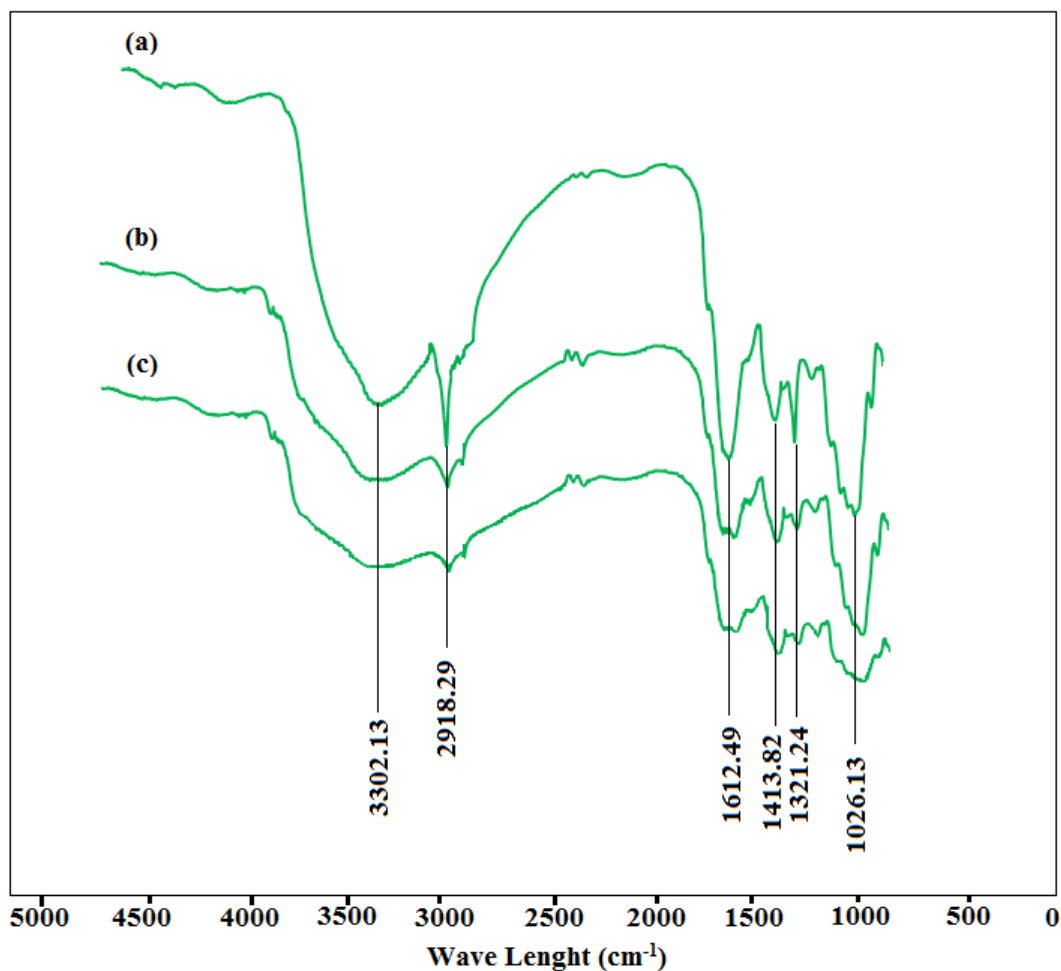


Figure 6.8: FTIR analyses using FIRR of (a) PWPP residue after hydrolysis in FIRR; (b) WPP after pretreatment; (c) raw WPP at optimal condition.

6.9. HPLC analyses of Hydrolyzed product:

High performance liquid chromatography (HPLC) system evaluated the quantitative analysis of produced glucose and other decomposition products arising through the hydrolysis process for both FIRRR and CHSBR at the optimal condition which is presented in **Fig. 14**. The retention times corresponding to glucose, fructose and 5-HMF were 8.413min, 13.376 min and 23.985 min respectively (*Namchot et al., 2014*). The concentration of the glucose was 89 mol% in which the glucose concentration (62mol %) was much higher than the fructose concentration (28mol %) whereas, the concentration of 5-HMF was relatively smaller (10 mol %).

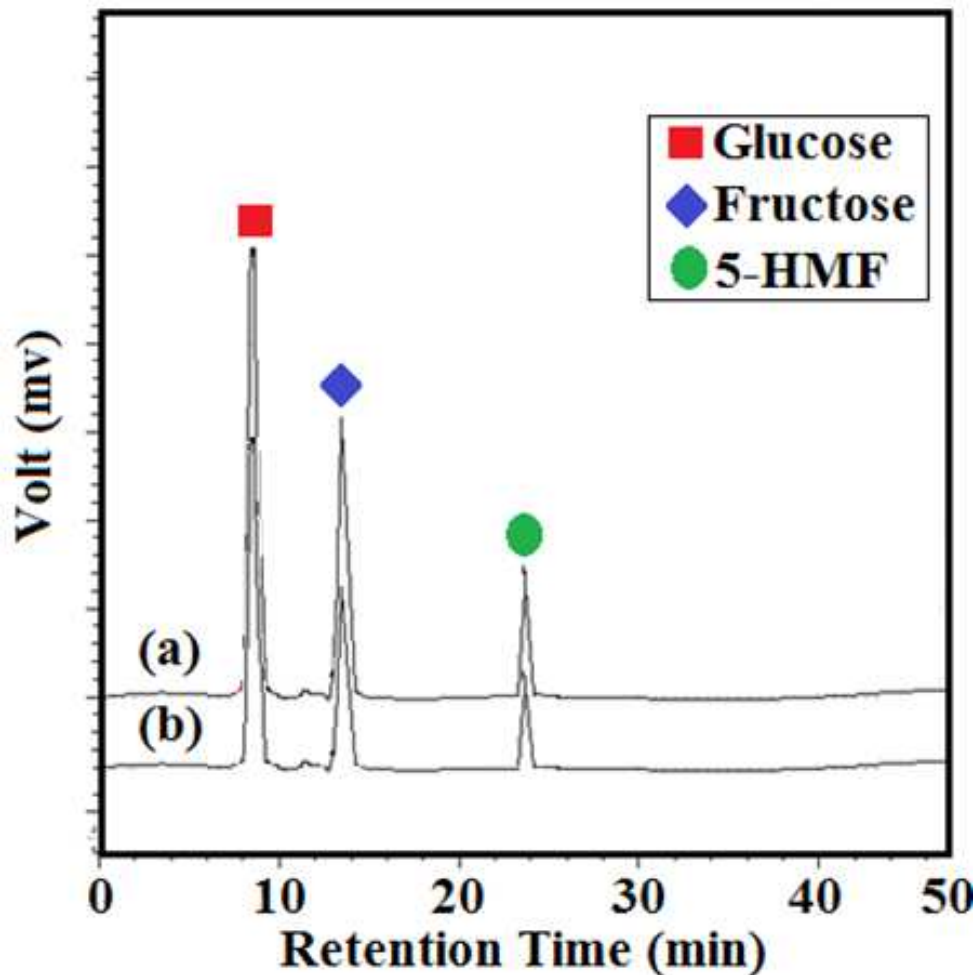


Figure 6.9:HPLC of hydrolyzed product conducted in (a) FIRRR; (b) CHSBR.

CHAPTER-7

CONCLUSION

7. Conclusion:

Thus, the infrared radiated one-pot batch reactor could demonstrate remarkable higher energy efficiency and productivity in terms of the desired glucose yield advocating its promising application in synthesis of fermentable sugar from waste lignocellulosic vegetable/ fruit resources in economically sustainable pathways. The present study demonstrates an efficient novel process to convert LB into glucose catalyzed by amberlyst-15 using an IRBR. A substantial reduction in batch time, and higher yield of the glucose at a considerably low temperature could be achieved in comparison with conventionally heated batch reactor. The Taguchi optimization method could effectively determine the optimal parametric values corresponding to maximum yield of glucose. The application of far infrared radiation not only accelerated the overall reaction but also this process can be performed at a minimum temperature level with shorter reaction time as compared to any other conventional heating and it improves to get the better yield of glucose. A significant amount of energy is saved (almost 27%) through the application of far infrared radiation in comparison with the conventional heating system. Present study also explores the valorization of waste through preparation of glucose by a cost effective and environmentally benign process. The method may also be exploited in the future for direct hydrolysis of LB into glucose and other chemicals.

CHAPTER-8

FUTURE SCOPE OF WORK

8. Future Scope of Work

- I. The hydrolysis reaction under FIR investigated in the present study may be conducted in a manner to facilitate production of 5-HMF, formic acid, levulinic acid by allowing for additional hydrolysis time to accomplish the series reaction.
- II. One pot pretreatment or hydrolysis of selected LB may be carried out in a semi-batch mode to achieve desired product strategy.
- III. We can produce bioethanol which is from these used feed stocks by fermentation technique. (as a direct substitute of petroleum based fuel, bio ethanol can be produced by fermentation of lignocellulosic biomass)
- IV. Process factors can be optimized further employing modern technologies like RSM (Response Surface Methodology), ANN (Artificial Neural Network) etc.

CHAPTER-9

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APPENDIX I:

Nomenclature List

OPERATING VARIABLES

Variables	Description
θ_T	Reactor Temperature
θ_t	Batch Time
θ_{np}	NH ₄ OH Loading
θ_{wp}	Water to PWPP Weight Ratio
θ_{pc}	Catalyst Concentration
Ω_g	Glucose Yield

SUPERSCRIPTS

Variables	Description
K	Kinetic Energy
r	Reaction Rate
A	Pretreated Papaya Peel
B	Water
C, g	Glucose
D	Undesired Product

SUBSCRIPTS

Variables	Description
i	Number of Repetitions
n	Number of Experiments Performed
t	Time
T	Temperature

STATISTICAL VARIABLES

Variables	Description
k_{CG}	Reaction Rate Constants for Glucose Formation
k_{DP}	Reaction Rate Constants for Glucose Degradation
E_{CG}	Activation Energy
E_{CG0}	Pre-Exponential Factor
C_B, C_A	Concentration of Water and PWPP, Respectively
C_{C0}	Glucose Concentration at Time Zero
C_C	Glucose Concentration
r_c	Glucose Production Rate

ABBREVIATIONS

Variables	Description
FIR	Far Infrared
FIRRR	Far Infrared Radiated Reactor
CHSBR	Conventionally Heated Stirred Batch Reactor
LB	Lignocellulosic Biomass
WPP	Waste Papaya Peel
PH	Pseudo-Homogeneous
PWPP	Pretreated Waste Papaya Peel
TOD	Taguchi Orthogonal Design
PHPF	Pseudo-Homogeneous Pseudo First
ANOVA	Analysis of Variance
XRD	X-Ray Diffraction
HPLC	High Performance Liquid Chromatography
FTIR	Fourier Transform Infrared Spectroscopy
AFEX	Ammonia Fiber Explosion

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10. RESEARCH ACTIVITY

Communicated Journal Paper

1. A full length paper entitled “**Intensified and energy efficient one-pot hydrolysis of waste papaya peels under infrared radiation: kinetics and Optimization of Glucose synthesis**” has been communicated to *chemical engineering journal* (Elsevier) 2016.
2. A full length paper entitled “**Far infrared radiated energy-proficient rapid one-pot green hydrolysis of waste watermelon peel: optimization and heterogeneous kinetics of glucose synthesis**” has been communicated to *RSC Advances* (Royal Society of Chemistry) 2016.

Conference Attended

3. Co-authored the paper entitled “**Progresses in Waste Biomass derived catalyst for production of Biodiesel and Bioethanol: A Review**” at 5th International Conference on Solid Waste Management at Indian Institute of Science, Bengaluru, India (**5th IconSWM 2015**).