The Effect of Pressure on the Dissolution of Cellulose in Ionic Liquids

by

Mohamed Farouk Bin Ibrahim (12660)

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

Supervisor: Dr. Muhammad Moniruzzaman
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CERTIFICATION OF APPROVAL

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Approved by:

_____

Dr. Muhammad Moniruzzaman

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
AUGUST 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHAMED FAROUK BIN IBRAHIM

ABSTRACT

The dissolution of cellulose in ionic liquids allows the comprehensive application of cellulose by combining two major green chemistry principles, which is by using bio-renewable feed-stocks and environmentally friendly solvents. In previous study by Rogers and co-workers, the dissolution of cellulose in ionic liquids required high temperature and high energy consumption. To overcome the high energy and temperature needed for dissolution, an idea was tinkled to conduct the dissolution in a pressurized cell. In this paper, the main objective is to study the pressure effect on the dissolution of cellulose in ionic liquids. Throughout the study, the pressure and temperature on dissolution of cellulose in ionic liquids were varied. The dissolution process were observed, the sample was later analysed with microscope and the dissolution time was taken. The controlling and varying value of the pressure and temperature significantly affect the dissolution time of cellulose. In this thesis, the findings show that as the pressure increase, the dissolution time decreases. The temperature also showed same behaviour, as the temperature increases, the dissolution time decreases. In conclusion, pressure does effects the dissolution rate and lower down the energy consumption for dissolution of cellulose in ionic liquids.

ACKNOWLEDGEMENT

First and foremost, thanks to God for His blessing and mercy in completing this one year project. It would befit to extend my outstretched gratitude to Dr. Muhammad Moniruzzaman, Chemical Engineering Department, Universiti Teknologi PETRONAS. It is a privilege to be under his supervision. Even with his tight schedules as lecturer and high commitment to Universiti Teknlogi PETRONAS, there was no moment where he fails to provide support and guidance. His advices and moral support gave a sense of strength and confidence in conducting the final year project.

Many thanks to our Final Year Project Coordinators, for their unlimited contributions success in providing the students with guidelines and seminars to enlighten hopes of confidence. Not forget to thank all lab executive and technicians as their willingness to provide the facilities and entertain our demand during conducting the project.

Last but not least, thanks to all the Universiti Teknologi PETRONAS involved lecturers and students who have been contributing great efforts and ideas making this final year project a success.

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CHAPTER 1
INTRODUCTION

1.1 Background Study

Cellulose is the most abundant natural polymer and has numerous applications in today's world [1]. The preparation of cellulose derivatives and their application have been described in many literatures [1,2,3]. Figure 1.1 below shows the cellulose structure where cellulose is a polydispersed in linear polyglucan which forms hydrogen-bonded supramolecule structures [16,18,23]. Recently, the cellulose-containing materials and their derivatives have been widely used in researches and society [4]. Some applications involve dissolution of cellulose, but it still has its limitations. Traditional cellulose dissolutions process are often expensive and require the use of unusual solvents, typically with high ionic strength and use relative in harsh condition [5,6,8]. Moreover, these traditional dissolution process sometime cause serious environmental problems due to the solvents cannot be recovered and reused [8].

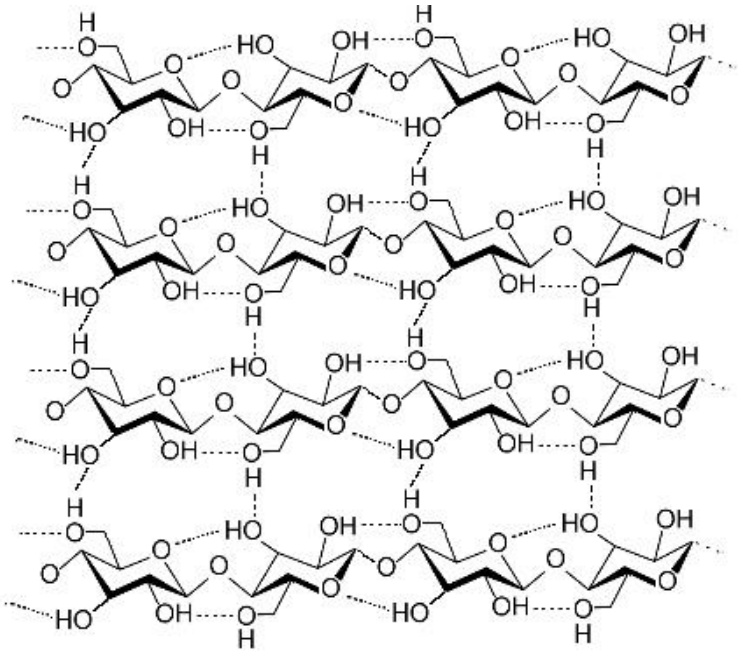
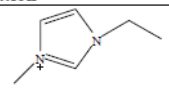
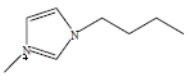
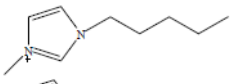
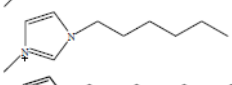
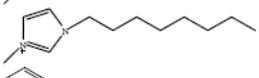
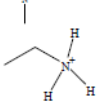
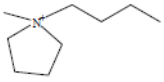


FIGURE 1.1. Cellulose structure.

In recent years, the "green" comprehensive utilization of cellulose resources has drawn much attention from governments and researches [6,7,9,10,14,27] . Therefore, to make full use of cellulose resources, it is essential to develop "green" cellulose extraction methods and suitable cellulose dissolution approaches.

Ionic liquids are a group of new organic salts that exist as liquids at a relatively low temperature (<100°C). They have many attractive properties, such as chemical and thermal stability, non-flammability and immeasurably low vapor pressure [4,15,30]. In contrast to traditional volatile organic compounds, they are called "green" solvents. Even in some studies have shown that cellulose can be dissolved in some hydrophilic ionic liquids [7]. Thus it has been proving a new platform for the "green" comprehensive utilization of cellulose resources. In this paper, an alternative green cellulose solvent was chosen which is 1-ethyl-3-methylimidazolium acetate [EMIM][Ac]. There are many types of ionic liquids, table 1 below shows some of the example of chemical formula and physical properties of ionic liquids that are available.

TABLE 1.1. Chemical and physical properties of ionic liquids.

Chemical formula		Abbreviation	Melting point, °C	Density (g mL^{-3}), 25 °C	Viscosity (cP), 25 °C	Molecular weight
Cation	Anion					
	$[BF_4]^-$	[EMIM][BF_4]	6	1.248	66	197.8
	$[PF_6]^-$	[EMIM][PF_6]	58-62	1.373	450	256.13
	$[BF_4]^-$	[BMIM][BF_4]	-82	1.208	233	225.80
	$[PF_6]^-$	[BMIM][PF_6]	10	1.373	400	284.18
	$[Br]^-$	[BMIM]Br	60	1.134	Solid	218.9
	$[Cl]^-$	[BMIM]Cl	89	1.120	Solid	146.50
	$[CF_3SO_3]^-$	[BMIM][CF_3SO_3]	16	1.290	90	260.0
	$[(CF_3SO_2)_2N]^-$	[BMIM] [$(CF_3SO_2)_2N$]	-4	1.420	52	487.9
	$[NTfO_2]^-$	[BMIM] [$NTfO_2$]	-8	1.404	48	433.0
	$[BF_4]^-$	[AMIM][BF_4]	-88	1.231	321	240.02
	$[BF_4]^-$	[HMIM][BF_4]	-82	1.075	211	254.08
	$[PF_6]^-$	[HMIM][PF_6]	-61	1.304	800	312.00
	$[BF_4]^-$	[OMIM][BF_4]	-79	1.11	440	281.8
	$[Cl]^-$	[OMIM][Cl]	0	1.000	16,000	230.50
	$[NTfO_2]^-$	[MPPyr] [$NTfO_2$]$^-$	0	1.44	39	416
	$[HCOO]^-$	BAF	-10	0.99	11.5	91
	$[NTfO_2]^-$	[BMPyrrol] [$NTfO_2$]	-50	1.4	71	422

The main purpose of this treatise is to decrease the temperature on dissolution of cellulose in an ionic liquid by increasing the reactor pressure. Throughout the study, the cellulose was analyzed based on a critical analysis of the intermolecular interactions involved and mechanisms of dissolution.

1.2 Problem Statement

The main problem rise due to the high temperature and energy needed in dissolution of cellulose in ionic liquids. Therefore, a specific study was planned by increasing the pressure for dissolution of cellulose. Thus, resulting in lowering down the consumption of energy needed to dissolve the cellulose in the ionic liquids. Other than that, by applying pressure during dissolution, the time consumption for dissolution process might be reduced as well. In this research, a High Pressure Solubility Measurement System (HPSMS) equipment was employed in order to conduct the dissolution of cellulose with ionic liquid in a pressurized cell condition.

1.3 Objective

The main objective of this research is to study on the effect of pressure and temperature on the solubility of cellulose in ionic liquid in the pressurized cell. Furthermore, the treated and untreated cellulose shall be characterized by using polarizing microscope after the dissolution process. After the dissolution process, the sample will be regenerated and analysed by using Field Emission Scanning Electron Microscope (FESEM), Thermogravimetric Analysis (TGA) and X-Ray Diffraction (XRD). Throughout the study, the ionic liquid used is 1-ethyl-3-methylimidazolium acetate [EMIM][Ac] and the cellulose used was commercial cellulose (Avicel cellulose) as the raw material.

1.4 Scope of Study

In this study, the main subjects under investigation are:

i. *The pressure will be varies from 10bar to 20bar for the dissolution process*
ii. *The temperature will be varies from 50 ^{o}C to 70 ^{o}C*
iii. *To lower the dissolution temperature down from 50 ^{o}C to the optimized temperature.*
iv. *Characterizing the treated and untreated cellulose by using microscope.*

1.5 Relevancy of the project

In dissolution of cellulose in the ionic liquids, high temperature and energy is needed in order forcing the ionic liquid to break the hydrogen bonds in the cellulose. Cellulose consist of long chain bio-polymer which is held by the hydrogen bonding. Ionic liquids in needed in order to dissolve the cellulose with help of the temperature and energy.

In order to reduce the temperature and energy needed in dissolution process, this project is conducted. The main objective of this project is to study the effect of pressure on the dissolution of cellulose in ionic liquids. The dissolution of cellulose in ionic liquid will be conducted in pressurized cell. When high pressure applied, thus resulting the temperature and energy needed for dissolution will be decreased and the dissolution time will be decreased. Finally, the objectives in reducing the temperature and energy needed for dissolution will be achieved.

1.6 Feasibility of the project within the scope and time frame

The student was given 29 weeks effective from 14th January 2013 to attach under Dr Muhammad Moniruzzaman, Chemical Engineering Department, Universiti Teknologi PETRONAS. Within approximately 7 month's duration for final year project, the student was given a project on the effect of pressure in dissolution of cellulose in ionic liquids.

Based on the knowledge in IT project management, the student has developed a well and organized Gantt's chart to conduct the project (refer methodology). By having regular formal and informal meetings and discussions with the supervisor and other lecturers, it helps the student to gather as much information on conducting the project.

As a conclusion, Gantt's chart and regular informal discussion will ensure the project to be on track and fulfil the objectives.

CHAPTER 2
LITERATURE REVIEW

As early as 1934, Graenacher discovered that molten N-ethylpyridinium chloride, in the presence of nitrogen containing bases, could be used to dissolve cellulose [11,26] . This might be the first examples of cellulose dissolution using ionic liquid. However, this was thought of little practical value because the concept of ionic liquid had not been put forward at the time. Until recently, the value of dissolution of cellulose with ionic liquid is re-evaluated based on the understanding of ionic liquid.

In 2002, Rogers and his group have carried out comprehensive studies on cellulose dissolution in ionic liquid and its regeneration [6,7,12,31]. Because of his great contribution, Roger has become a winner of the 2005 US presidential Green Chemistry Challenge Awards. Zhang and his co-workers have also conducted extensive research in this field [8,9,15].

Cellulose is whether it is refined or natural, can be dissolved, without deviation, in some hydrophilic ionic liquids such as [EMIM][Ac], [EMIM][Cl], [BMIM][Cl], and [AMIM][Cl]. Cellulose solubility and the solution properties can be controlled by selection of the ionic constitute. Figure below shows the structure of the cellulose.

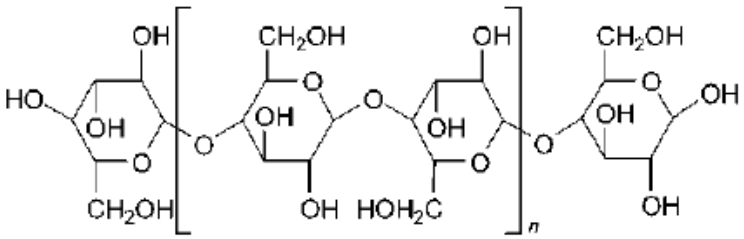


FIGURE 2.1. A cellulose polymer chain, *n* is typically 400 – 1000.

In his study, Rogers stated that the microwave heating can significantly accelerate its dissolution [17,25]. The high chloride concentration and activity which is assumed highly effective in breaking the extensive hydrogen-bonding network presence in cellulose, plays an important role in its dissolution. The presence of water in IL greatly decrease the solubility of cellulose through competitively hydrogen-bonding its micro fibrils [6,7]. Table 2.1 summarizes the results obtained using high MW dissolving pulp (DP $\approx$ 1000).

TABLE 2.1. Solubility of Dissolving Pulp in Ionic Liquds.

ionic liquid	method	solubility (wt %)
$[C_4mim]Cl$	heat (100 °C)	10%
	(70 °C)	3%
$[C_4mim]Cl$	heat (80 °C) + sonication	5%
$[C_4mim]Cl$	microwave heating	25%, clear
	3−5-s pulses	viscous solution
$[C_4mim]Br$	microwave	5−7%
$[C_4mim]SCN$	microwave	5−7%
$[C_4mim][BF_4]$	microwave	insoluble
$[C_4mim][PF_6]$	microwave	insoluble
$[C_6mim]Cl$	heat (100 °C)	5%
$[C_8mim]Cl$	heat (100 °C)	slightly soluble

Cellulose is disordered in its ionic liquid solution and this cellulose solvation process was confirmed at the atomic level by high-resolution C NMR studies [13]. When high concentration of cellulose (>10 wt%) are dissolved in ionic liquid, the liquid crystalline solutions of cellulose which are optically anisotropic between crossed polarizing filters and displays birefringence, are formed [6,7].

Cellulose in its ionic liquid solution can be easily precipitated by addition of water, ethanol or acetone. The regenerated cellulose has almost the same degree of polymerization and polydispersity as the initial one, but its morphology is significantly changed and its micro fibrils are fused into relatively homogeneous macrostructure.

In changing the regeneration process, the regenerated cellulose can be in a range of structural forms, such as powder, tube, beard, fiber or film. The regeneration process also has an impact on the regenerated macrostructure. The degree of crystallinity of the cellulose can be manipulated during its regeneration and the cellulose with micro-crystallinity varying from amorphous to crystalline can be obtained under different regeneration conditions. Figure 2.2 below shows SEM micrograph of initial dissolving pulp and after dissolution and regeneration. It shows that the structure was deformed after treated.

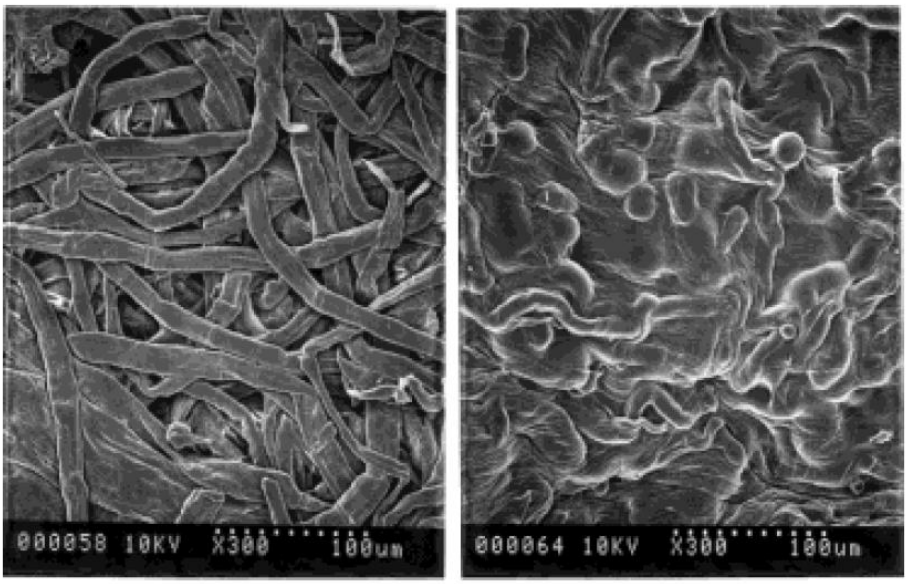


FIGURE 2.2. SEM micrographs of the initial dissolving pulp (left) and after dissolution in [C4mim]Cl and regeneration into water (right).

The store time of the cellulose-ionic –liquid solution also affects the regenerated cellulose micro-structure. The amorphous cellulose can be obtained after the cellulose –ionic-liquid solution is stored for a few weeks [6]. The ionic liquid can be recovered and reused after cellulose regeneration. Various method, such evaporation, ionic exchange, pervaporation, reverse osmosis and salting out are used to recover ionic liquid [12].

The dissolution of cellulose using ionic liquids has been providing a new platform for “green” cellulose utilization. It also provides the possibilities of comprehensive utilization of lignocellulosic materials by fractionation of the lignocellulosic materials with “green” means.

This might bring the breakthrough in production of such basic chemical feed-stock as ethanol and lactic acid from lignocellulosic materials and reduce society's dependent on non-renewable petroleum-based feed-stocks. A new avenue is opened for solving the environment mental and energy problems to maintain sustainable development.

Besides the comprehensive "green" utilization of lignocellulosic materials, it also provides the possibilities of preparation of various advanced materials, including cellulose derivatives and cellulose composites, in place of the synthetic polymers, which biodegrade slowly.

In fact, some of the above mentioned cellulose derivatives and cellulose composites have great potential in industrial applications. For example, the wool keratin/cellulose composite could be used in the textile industry to produce fibers. Although lots of basics studies, such as economical syntheses of ionic liquids and studies of the ionic liquid toxicology, are much needed, commercialization of these processes has made great progress in recent years.

In China, the institute of Process Engineering, Chinese Academy of Sciences and Wuliangyi Corporation has jointly launched a program to produce an anti-bacterial fiber using the wool keratin/cellulose composite technology. BASF has also just taken out a license on the technology developed by Rogers for industrial production of some advanced materials [7]. It is quite clear that commercialization of these processes will take place in the near future and we will benefit a lot from these technologies.

CHAPTER 3
METHODOLOGY

3.1 Research Methodology

The methodology for conducting this research project is by using experimentation and analytical skills. As this project is mainly an empirical research, the results obtained from this research can be used to compare with other literature results. In advance, result obtained from this project by using different configuration of operating parameters and various types of ionic liquids to dissolve cellulose can be used as a basis of comparison with other works done. The results can further enhance the research and development of the dissolution of cellulose in ionic liquid. The project activities in this research are mainly experimental work. After thorough literature review is done, experimental works can be conducted to investigate the effect of pressure on dissolution of cellulose in ionic liquid.

3.2 Experimental Procedures/Approach

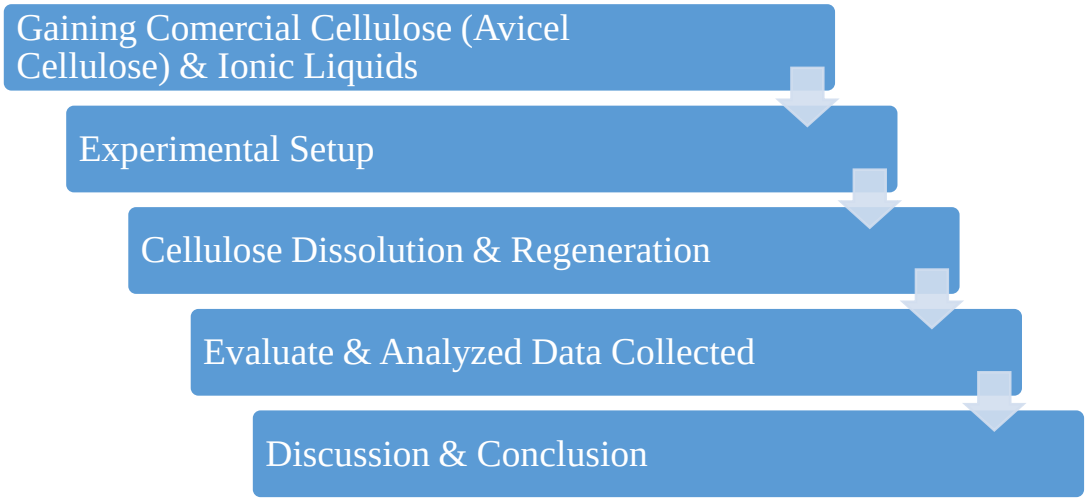


FIGURE 3.1. The schematic diagram depicting the general approach in this project.

3.2.1 Raw Materials and Chemicals Needed

In the experiments that are going to be conducted, several raw materials and chemicals are needed. There are:

i. Avicel Cellulose
ii. Ionic Liquids – 1-ethyl-3-methylimidazolium acetate [EMIM][Ac]
iii. Methanol – Used to clean up the equipment and apparatus after experiment
iv. Dimethyl Sulfoxide (DMSO) – As a diluent for ionic liquids
v. Acetone – anti-solvent for regeneration
vi. Water – for washing purpose

3.2.2 Detailed Research Methodology

A) Gaining Commercial Cellulose (Avicel Cellulose) and Ionic Liquids:

1. The commercial cellulose (Avicel cellulose) will be ordered from the supplier, Sigma Aldrich.
2. Ionic Liquid which is [EMIM][Ac] will be purchased as for the solvent in dissolution of cellulose.

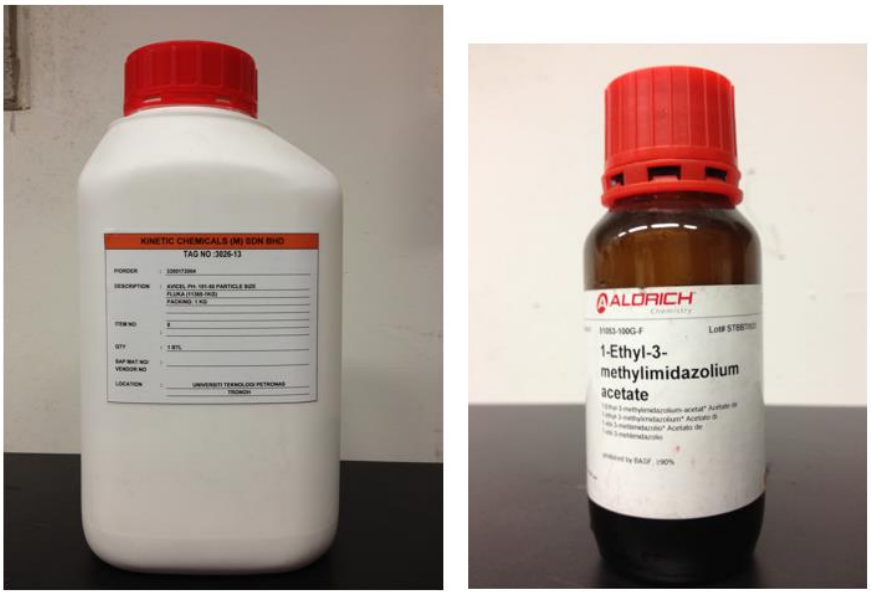


FIGURE 3.2. Commercial Avicel cellulose (left) and [EMIM][Ac] (right).

B) Experimental Setup:

1. High Pressure Solubility Measurement System was employed in order to conduct the study.
2. A safety briefing was given by the lab technologist at the beginning of the familiarization session.
3. Hands on tutorial and practical was conducted with equipment technician on operating the HPSMS equipment.

C) Cellulose Dissolution:

1. Avicel cellulose (5% wt) is dissolve with ionic liquids in [EMIM][Ac] and addition of DMSO as for ionic liquid diluent.

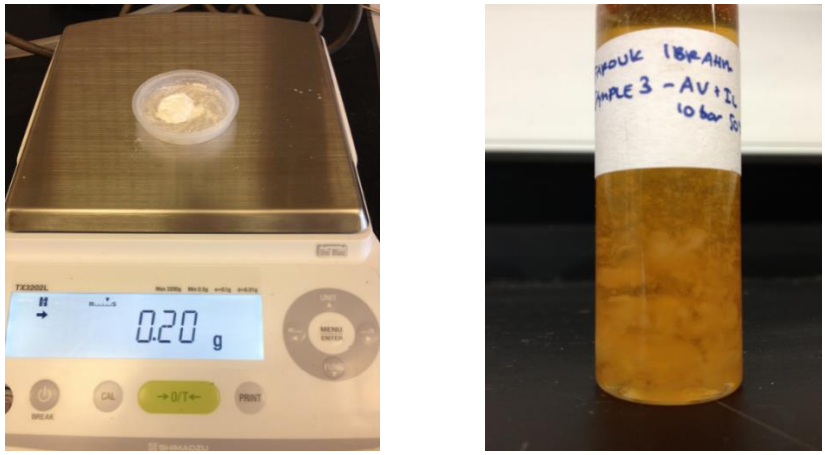


FIGURE 3.3. 5 wt% avicel cellulose before (left) and after (right) mixture with [EMIM][Ac] and DMSO.

2. The mixtures will be maintained at the different ranges of temperature (50^{o}C – 70 ^{o}C) and pressure (10 – 20 bar) for definite period of time.
3. High Pressure Solubility Measurement System (HPSMS) is employed in order to systematically analyze the effects of pressure and temperature in the range of 50 ^{o}C – 70 ^{o}C on the solubility of cellulose in ILs.
4. Nitrogen gas was pumped into the system by using a compressor. Therefore a pressurized system was created.

FIGURE 3.4. Sample is in the pressurized reactor (left) and the HPSMS control panel (right).

4. A few drops of pressurized dissolution sample were taken out in every two hour interval for analyzing purpose.
5. The samples were analyzed by using a microscope to determine the treated and untreated cellulose in the dissolution.

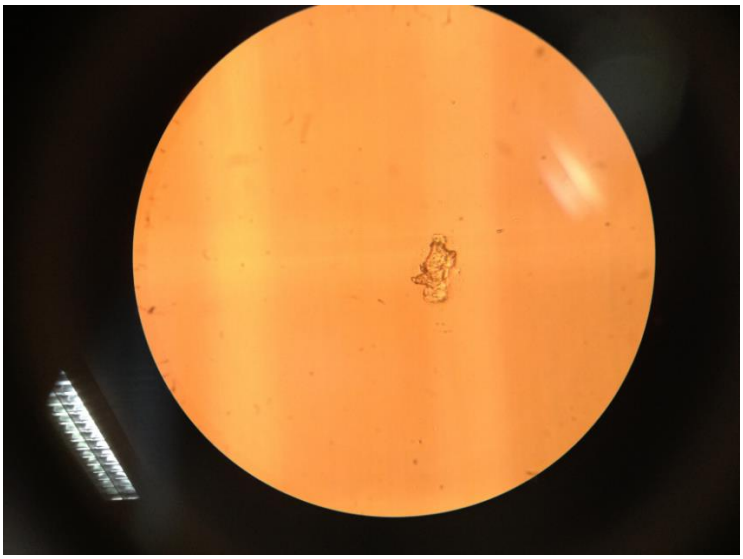


FIGURE 3.5. Avicel cellulose structure under microscope view.

D) Cellulose Regeneration:

1. Acetone will be used sufficiently to recover regenerated cellulose from ILs.
2. The reaction mixture will be kept at room temperature a few minutes to cool down in order to prevent quenching.
3. Acetone will be slowly added to the reaction mixtures and this acetone added mixture will be stirred for few minutes.
4. After the stirring, the sample will be left at room temperature and regenerated cellulose is allowed to precipitate,
5. The supertenant will be removed by filtration of the sample with glass filter paper.

FIGURE 3.6. Sample is being filtrate by using vacuum pump.

6. The filtrate, regenerated cellulose, was washed 5 - 10 times with the acetone for removal of IL as much as possible.

7. Washed regenerated cellulose will be left at 60ºC for 12 - 24 hours until the excess amount of water is removed.

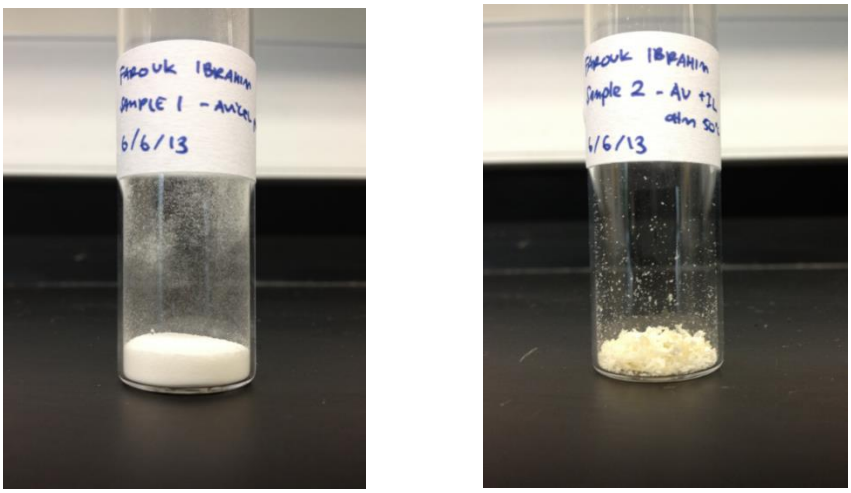


FIGURE 3.7. Avicel cellulose before (left) and after (right) treatment with pressure and regenerated.

E) Evaluate and analyzed data collected

1. The samples that were collected will be analyzed by microscope to determine the treated and untreated cellulose after its dissolution.

2. Evaluate the structural differences between regenerated cellulose samples obtained at different operation conditions by Polarizing Microscope, Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA) and X-Ray diffraction analyses (XRD).

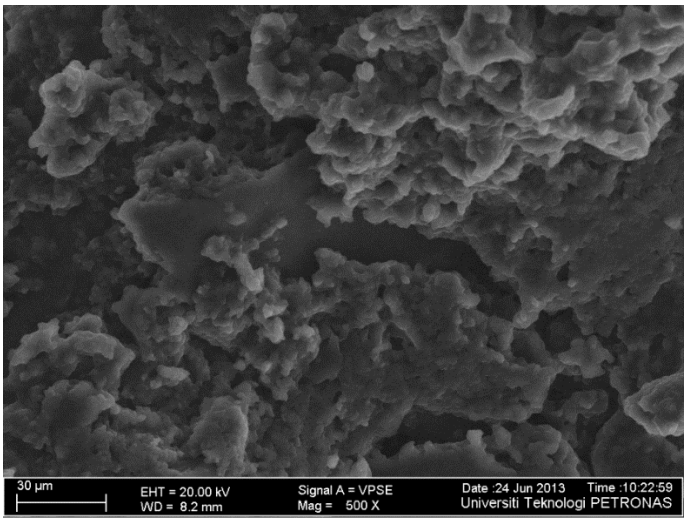


FIGURE 3.8. Avicel cellulose under SEM morphology.

3. Data was collected and statistical approach will be employed to determine and specify the optimum pretreatment condition for cellulose considering the effect of several parameters such as the pressure and temperature.

F) Discussion and Conclusion

1. The results and findings throughout the study will be discussed, conclude and compiled.

2. A final report on the effect of pressure in dissolution of cellulose in ionic liquids will be produced.

3.2.3 Equipment:

Throughout the project, the equipment that will be used is High Pressure Solubility Measurement System (HPSMS). Figure 3.9 below shows the HPSMS equipment and its P&ID.

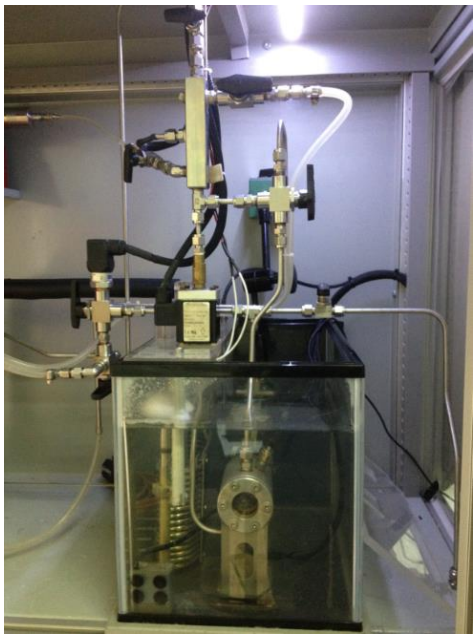


FIGURE 3.9. High Pressure Solubility Measurement System (HPSMS)

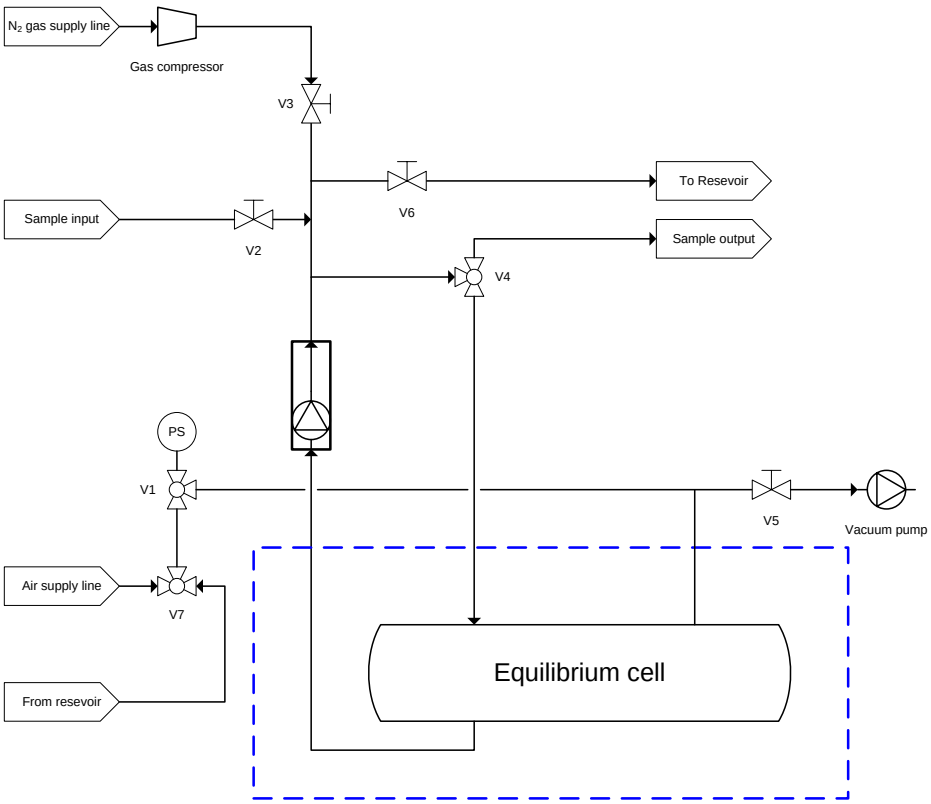


FIGURE 3.10. High Pressure Solubility P&ID diagram.

Other type of facilities that are needed:

1) Microscope:
   To determine the treated and untreated cellulose
2) Scanning Electron Microscopy (SEM):
   To observe the homogeneous microstructure of regenerated cellulose
3) X-ray diffraction analyses (XRD): *to be conducted on 20 August 2013
   To determine the degree of crystallization of regenerated cellulose
4) Thermogravimetric Analysis (TGA): *still in waiting queue
   To determine the physical and chemical changes on the cellulose before and after pressurized.

3.2.4 Variation of factors

As mentioned previously in Chapter 1, there are 2 subjects that are being investigated.

1) To study the effects of pressure and temperature on the solubility of cellulose in ionic liquid
2) To characterized the treated and untreated cellulose.

3.2.5 Characterization of raw material and product

Characterization of raw material Avicel Cellulose is necessary as it can be used as a basis to compare with other types of biomass. The main characteristics of Avicel cellulose that are evaluated are:

i. Temperature & pressure dissolution completion
ii. Reaction time
iii. Degree of crystallization of the cellulosic material
iv. Regenerated cellulose yield
v. Water content of biomass

The characterization of ionic liquid used:

i. Cost of ionic liquids
ii. Water content
iii. Purity of the ionic liquid

3.3 Project Activities

At the beginning of the project, a supervisor was allocated and a topic was given to the student. Preliminary research work and literature review was made at the beginning of the semester. The literature and journals read were critically analyzed. To ensure the quality of the literature, recentness of the literature plays an important role as Rogers & co-worker wrote many journal ever since 2002.

After some reading and writing was made, the student will have his oral proposal defence in the week 8. The proposal defence was a success and the project was accepted. After the proposal defence, the student have submitted requisite forms on the chemicals needed for the experiment. Avicel cellulose and ionic liquids [EMIM][Ac] was ordered and the requested chemicals will be received in two to three weeks' time.

In the meantime, High Pressure Solubility Measurement System (HPSMS) was employed. This equipment was loan from the Biohydrogen Laboratory at Block P, UTP. The laboratory items loan form was submitted and the application was approved. Figure below shows the HPSMS equipment that had been employed.

FIGURE 3.11. High Pressure Solubility Measurement System (HPSMS) equipment.

After the application on HPSMS equipment was approved, the student have a session on the equipment/lab familiarization. A briefing on the equipment was given by Mr Reza, lab staff at block P at the beginning of the lab familiarization. Later, a hands on tutorial on running and troubleshooting session of the equipment was conducted by Mr Guan, technologist from Dixson. From this sessions of familiarization on the HPSMS, the student now are allowed to conduct the dummy experiment.

The first dummy experiment was conducted at week 10. Water was used as the sample, 50ml, at the pressure of 8 bar and 45 ^{o}C. In this session, water was pressurized for about two hours. The main objective of this experiment is to see the temperature and pressure consistency in this equipment. Figure below show how is the condition of the water inside the pressurized cell and the sample of water collected after the completion on the dummy experiment

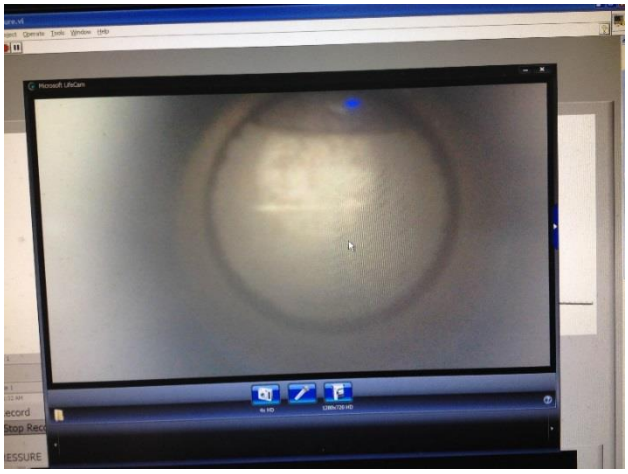


FIGURE 3.12. Condition of water sample inside the pressurized cell.

FIGURE 3.13. A sample water collected after the completion on dummy experiment.

During the two hours, the temperature and pressure was observed and it shows a consistency readings for two hours. Figure below shows the HPSMS software interface.

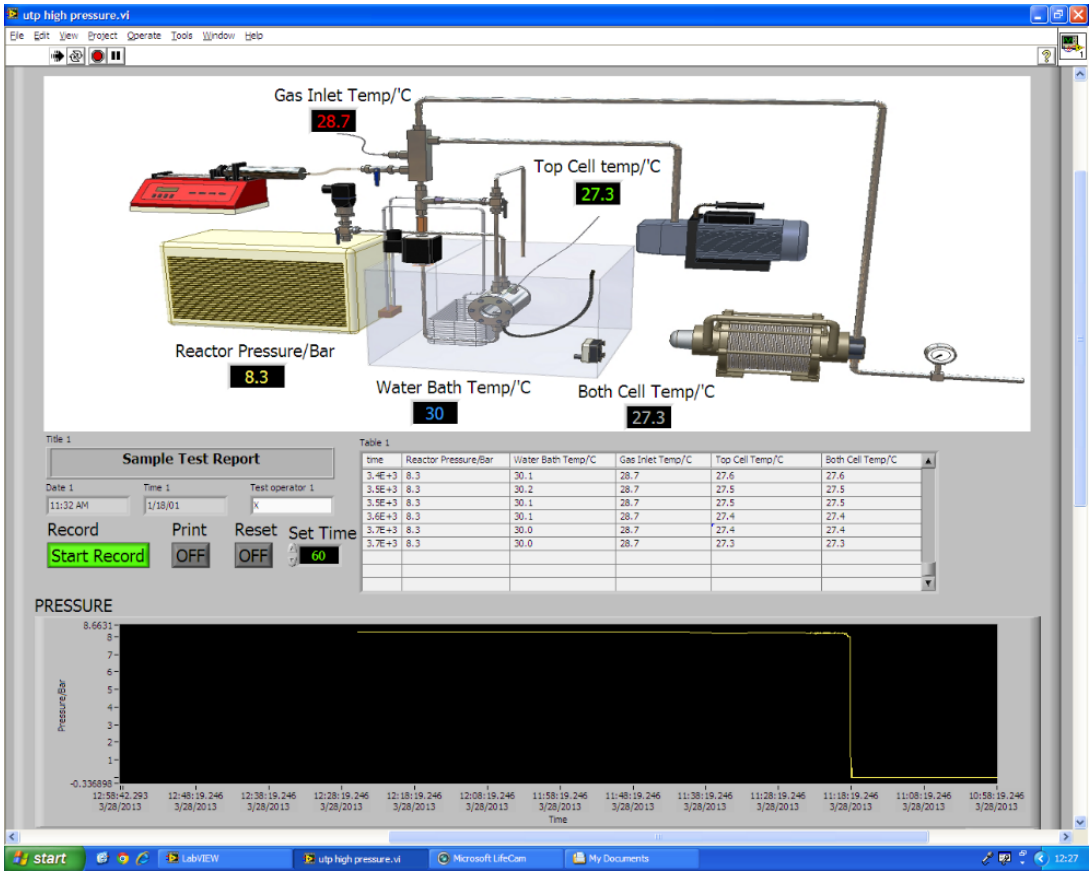


FIGURE 3.14. HPSMS simulation interface.

In week 11, another dummy experiment was conducted. In this experiment, a 5 wt% of wood powder was added to the water solution. The temperature and pressure at 30 ^{o}C and 8 bar. The experiment was conducted for two hours and the temperature and pressure readings show a consistence set of data as shown below.

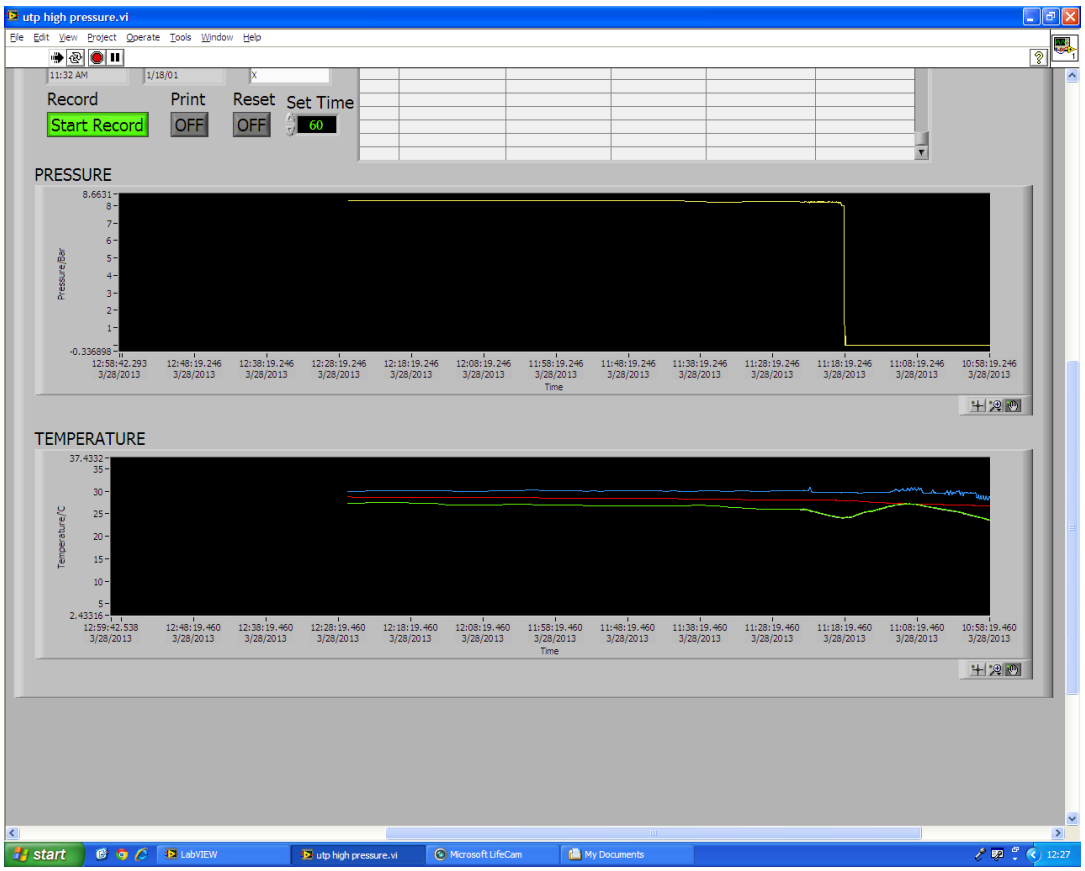


FIGURE 3.15. Consistency temperature and pressure data shown in HPSMS simulation.

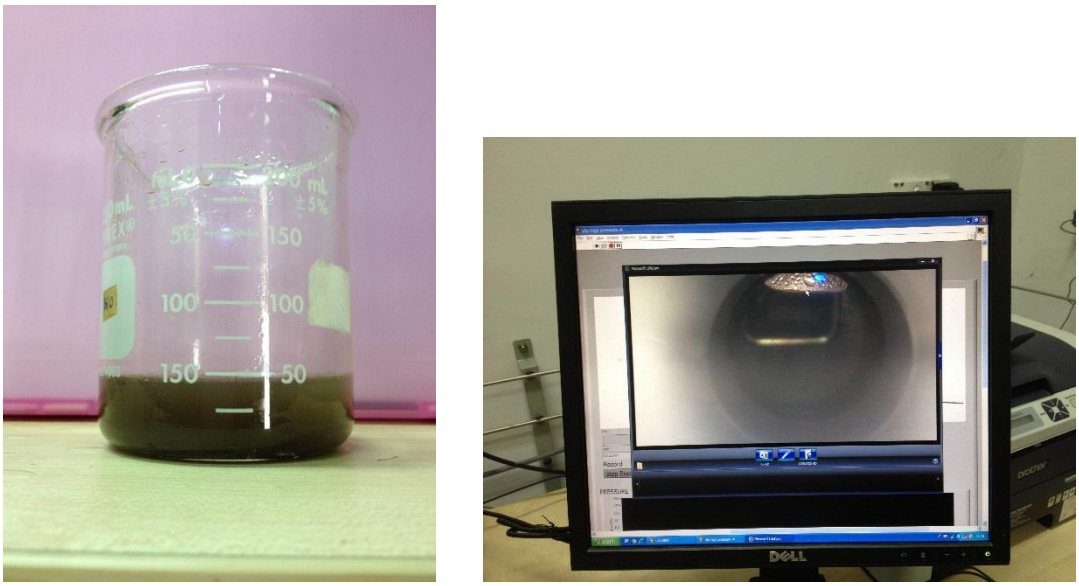


FIGURE 3.16. Mixture of dried wood powder with water for dummy experiment.

The objective of this dummy experiment was achieved. The student knows how to operate the HPSMS equipment based on the standard operating procedure (SOP). The temperature and pressure consistency readings also shown a great response throughout the experiment.

On the week 13, a presentation was made under Dr Suzana request with Dr Muhammad Moniruzzaman supervision, a discussion on the future experiment was touched. Control variables such pressure (10-20 bar), temperature (50-70 ^{o}C) and type of ionic liquids [EMIM][Ac] was set. As for constant variables, the cellulose was set to 5 wt%. The response variables for the experiment was to determine the dissolution time, yield of regenerated cellulose and the degree of crystallization of cellulose. Table below shows the experiment matrix that have been discussed on the presentation.

TABLE 3.1. Sample table for Run 1.

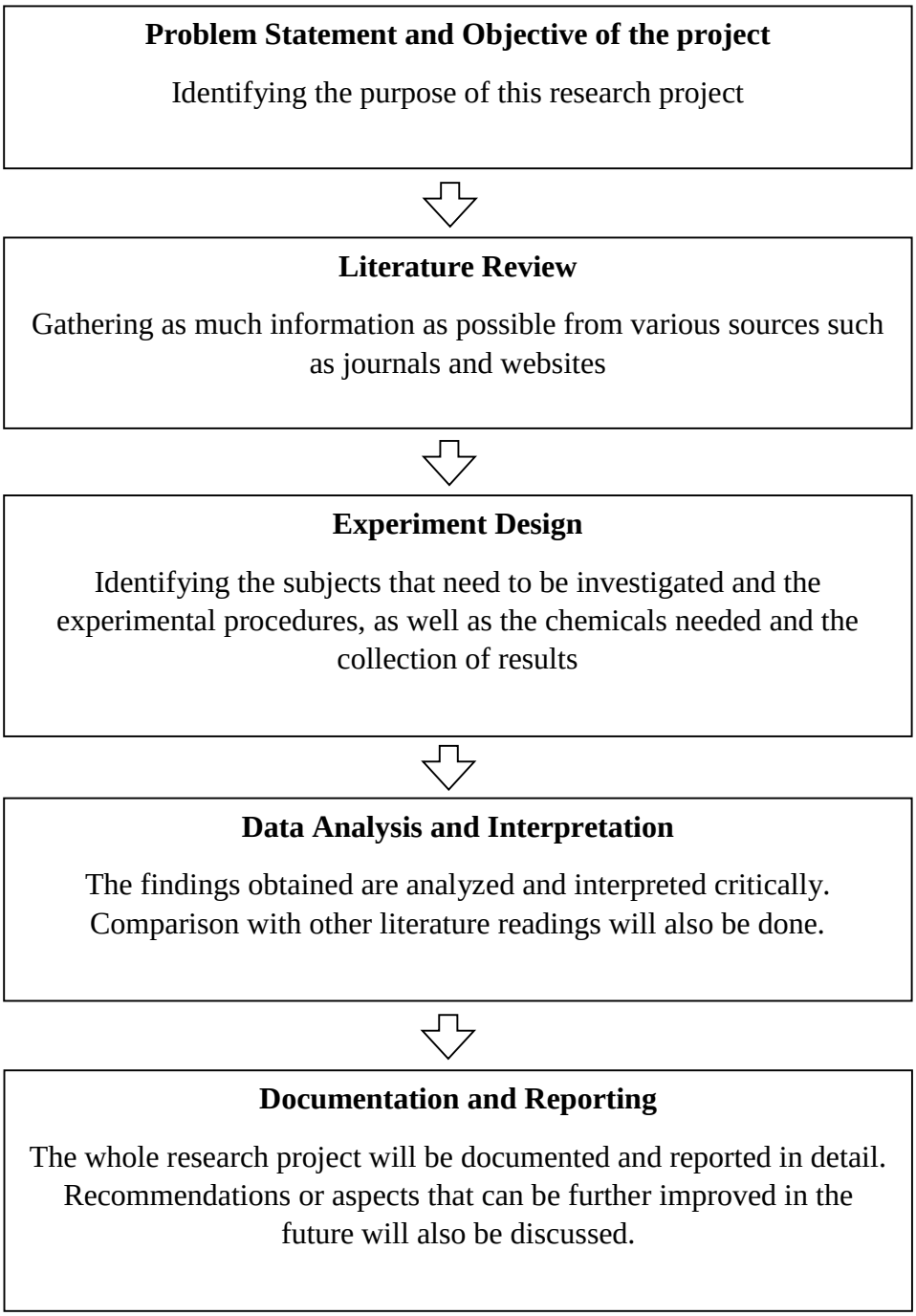
Run	Cellulose (wt%)	Pressure (Bar)	Temperature (^{o}C)	Time (Hour)	Sample No
1	5	10	50	2	Sample 1
	5	10	40	4	Sample 2
	5	10	40	6	Sample 3
	5	10	40	8	Sample 4

Table above shows the sample experiment matrix on the first run on the experiment. The temperature and pressure will be set at 50 ^{o}C and 10 bar with 5 wt% cellulose. There are four sample that will be taken out from the reactor cell at every two hour interval. The sample set of experiment matrix will be applied to other sets of runs with different pressure, temperature, and cellulose concentration.

The collected sample will be observed under microscope, FESEM, TGA and XRD for analyzing the dissolution of cellulose in the ionic liquids. The dissolve cellulose will be compared on their structure, dissolution time, and yield and degree of crystallization.

3.4 Key Milestones

Several key milestones for this research project must be achieved in order to meet the objective of this project:



3.4.1 Study Plan (Gantt Chart) – FYP1

NO	DETAIL / WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Title	■	■													
2	Preliminary Research Work and Literature Review		■	■	■	■	■									
3	Submission of Extended Proposal Defence							●								
4	Preparation for Oral Proposal Defence							■								
5	Oral Proposal Defence Presentation									■						
6	Equipment/Lab Familiarization										■	■				
7	Sample Gathering										■	■	■			
8	Conducting Dummy Experiment											■	■	■		
9	Preparation of Interim Report													■	■	
10	Submission of Interim Draft Report														●	
11	Submission of Interim Final Report															●

● Suggested milestone

■ Process

3.4.2 Study Plan (Gantt Chart) – FYP2

NO	DETAIL / WEEK	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Lab Preparation	■															
2	Lab Process – Experiment Run 1		■														
3	Lab Process – Experiment Run 2			■													
4	Lab Process – Experiment Run 3				■												
5	Lab Process – Experiment Run 4					■											
6	Lab Process – Experiment Run 5						■										
7	Submission of Progress Report							●									
8	Process work continuous (Labs/Experiments)									■	■	■	■	■			
9	Pre-SEDEX											●					
10	Submission of Draft Report												●				
11	Submission of Dissertation (soft bound)													●			
12	Submission of Technical Paper													●			
13	Oral Presentation														●		
14	Submission of Dissertation (hard bound)																●

● Suggested milestone

■ Process

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Data Gathering and Analysis

The dissolution of cellulose in the ionic liquid [EMIM][Ac] assisted with pressure were studied. The pressure were varied from 10 bar to 20 bar throughout the study. Later, a microscope was employ to monitor the variation of the cellulose during the dissolution process to determine the complete dissolution of cellulose in [EMIM][Ac]. The dissolution process takes place for few hours and the dissolution effects were captured under a microscope as shown in figure 4.1 below.

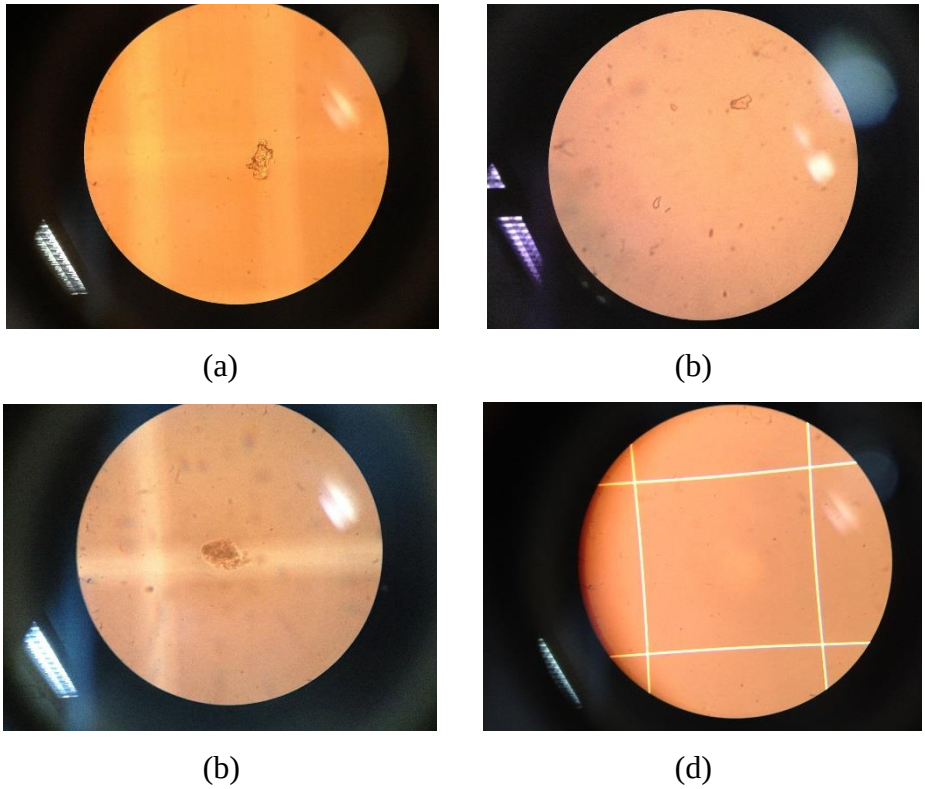


FIGURE 4.1. Images of Avicel cellulose with 5wt% dissolved pressurized cell at 15 bar in [EMIM][Ac] at 50^{o}C for 0 hour (a), 2 hour (b), 4 hour (c), and 6 hour (d).

It could be seen that at the beginning of dissolution in [EMIM][Ac], there was a clear bright shot (Fig. 4.1.a) of a cellulose structure under the microscope, which was due to presence of extensive crystalline structure in initial avicel cellulose. As the dissolution time increased, the eyeshot of the microscope turned gloomy. Fig. 4.1.b shows the viewing field of the cellulose suspension obtained after pressurized for 2 hours with 15 bar. It shows that the cellulose are partially dissolved in [EMIM][Ac]. Some large cellulose burst into smaller in size due to the pressurized effect. After 4 hours of pressurized dissolution, the large cellulose starts to burst into smaller size. This shows that the effect of pressure had cause the cellulose to dissolve in [EMIM][Ac]. After 6 hours of pressurized dissolution, as shown in fig 4.1.d, there are small cellulose structure that remained as visible. Due to only small cellulose structure remaining, we can assume at 6 hours pressurized dissolution, the Avicel cellulose is completely dissolved and highly dispersed in [EMIM][Ac].

On the next step for analysis, Field Emission Scanning Electron Microscope (FESEM) analysis was conducted on to the sample. The main objective of FESEM analysis is to observe the morphology of the treated and untreated cellulose under pressurized system. The sample analysed was taken from sample number 2 where the pressure was set to 10 bar at 50 ^{o}C with 5 wt% of cellulose dissolved inside the ionic liquid. Figure below shows the comparison of the cellulose structured before and after treatment.

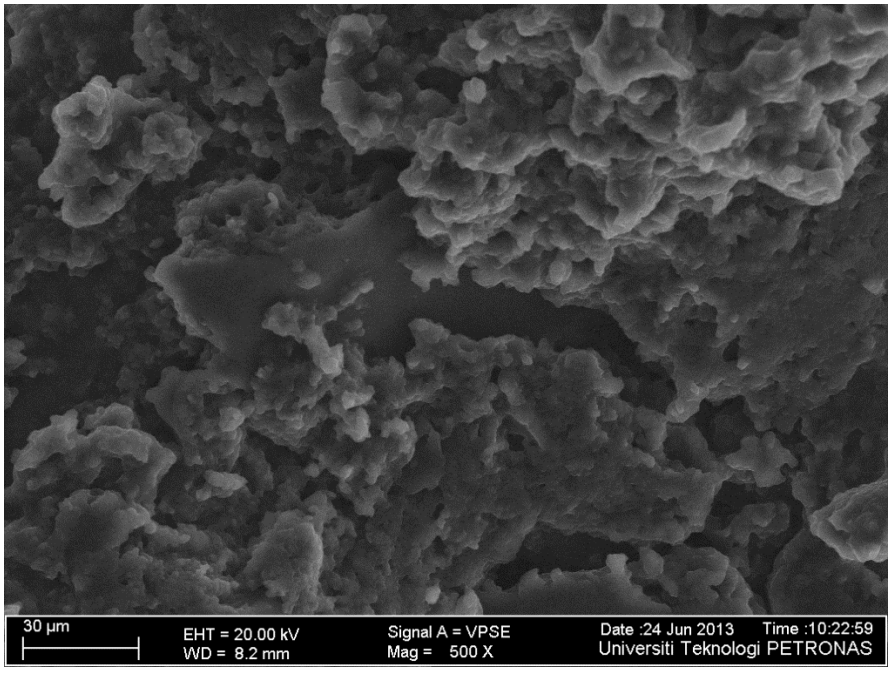


FIGURE 4.2. Avicel cellulose morphology before pressurized. (500x)

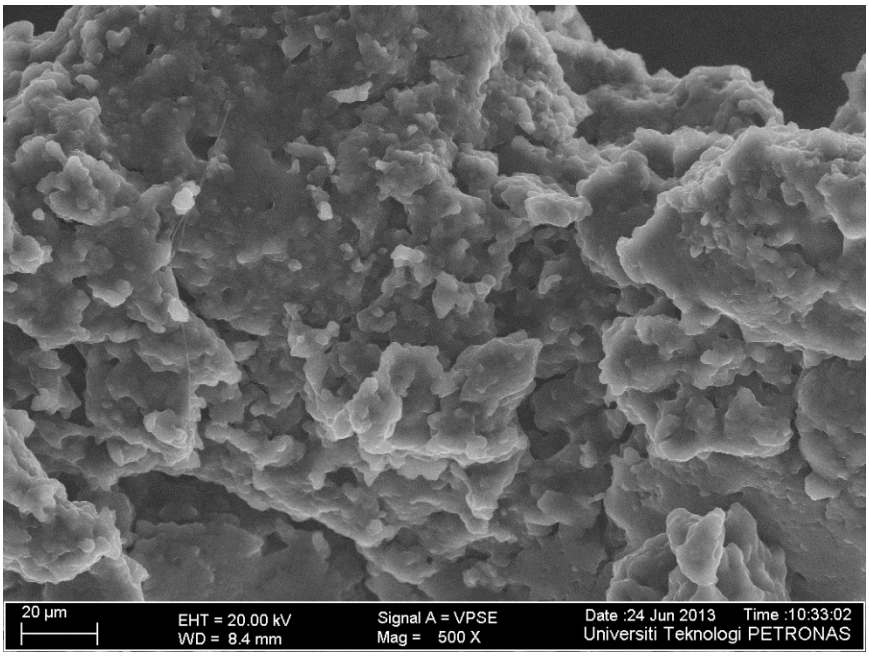


FIGURE 4.3. Avicel cellulose morphology after pressurized at T= 4 hours. (500x)

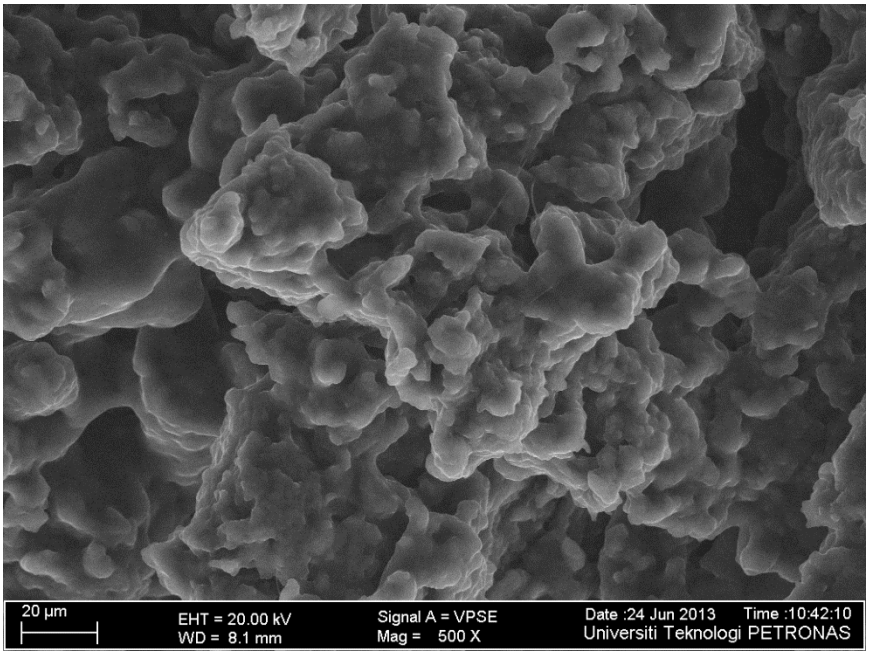


FIGURE 4.4. Avicel cellulose morphology after pressurized at T= 8 hours. (500x)

FESEM analysis shows that as the pressure is applied, the structure of the avicel cellulose is deformed. In Figure 4.2, it shows that the cellulose have more edges structure compared to others. In Figure 4.3 and 4.4, the edges becomes smoother. It can be compare where, as the dissolution time is increased, the cellulose structure becomes smoother. This is because the pressurized system during the dissolution of the cellulose in ionic liquid helped the ionic liquid to penetrate and dissolve the cellulose in the ionic liquid. The hydrogen bond were broken with the assist of the pressure and temperature supplied to the system. Resulting the deform structure of the cellulose.

Figure below shows a higher magnification of 2000x on the cellulose structure before and after treatment.

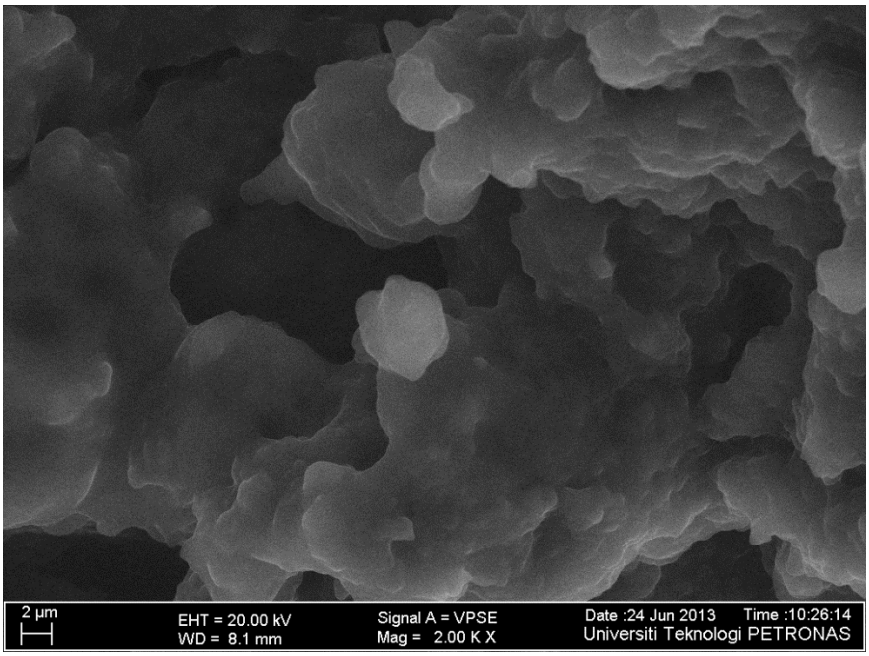


FIGURE 4.5. Avicel Cellulose before pressurized. (2000x)

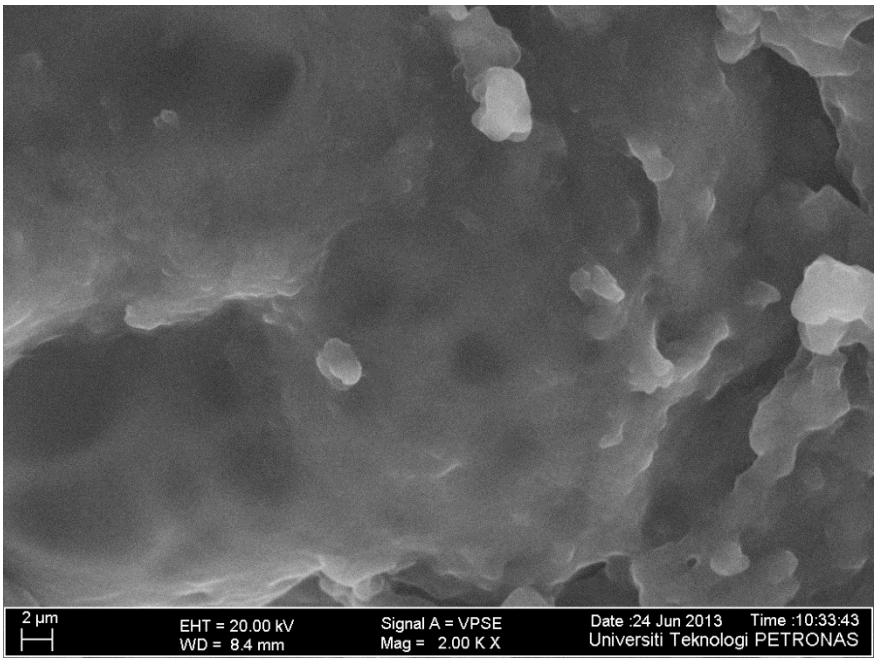


FIGURE 4.6. Avicel Cellulose after pressurized at T= 4 hours. (2000x)

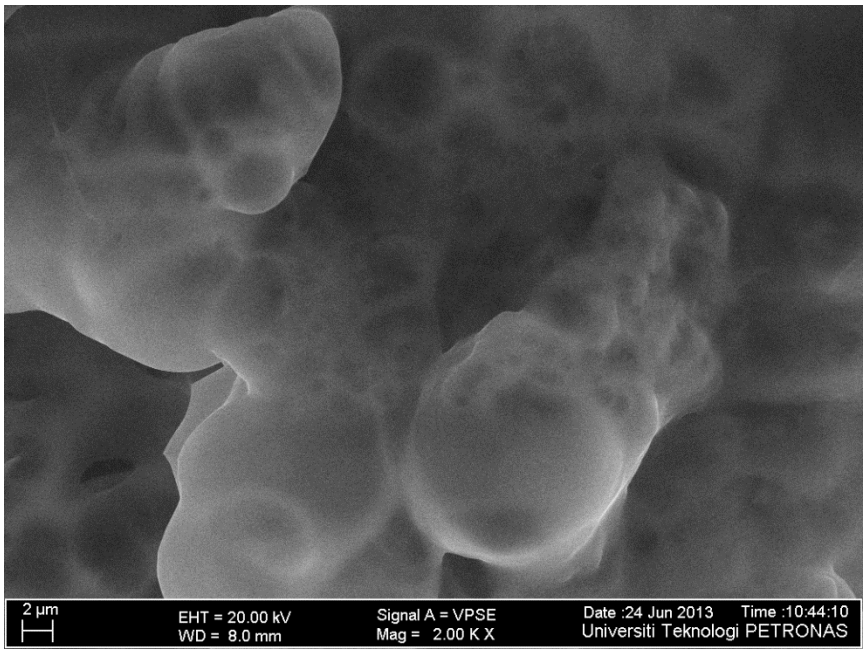


FIGURE 4.7. Avicel Cellulose after pressurized at T= 8 hours. (2000x)

4.2 Experimentation/Modelling

Table 4.1 shows the list of the pressurized dissolution experiments conducted at 50^{o}C with various pressure and cellulose concentration. As shown in table 4.1, as the weight percent of avicel cellulose increased, the dissolution time increases. The increment of the dissolution time is due to the weight percent of avicel cellulose increased from 5 wt% to 10 wt% resulting more mass transfer occurred between cellulose particles and ionic liquid.

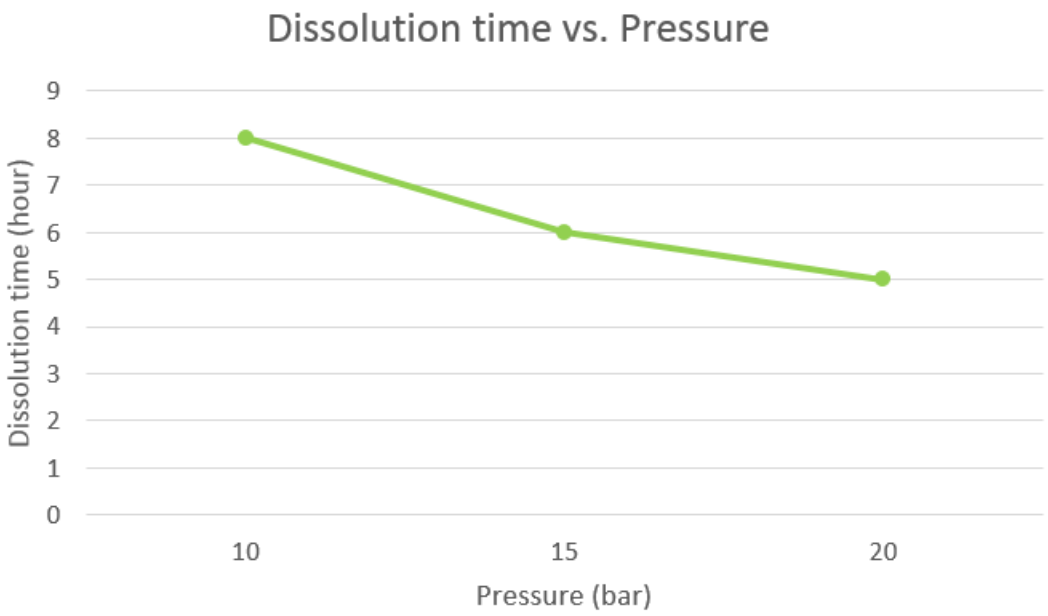
TABLE 4.1. Dissolution time respected with pressure, temperature and weight percent variance.

Dissolution conditions				
Sample no.	Weight percent (wt%)	Temperature (^{o}C)	Pressure (bar)	Dissolution time (hour)
1	5	50	1	-
2	5	50	10	8
3	10	50	10	16
4	5	50	15	6
5	5	50	20	5
6	5	60	20	4
7	5	70	20	3

It was obvious that the pressure had beneficial effect on cellulose dissolution. As the pressure is increased from 1 bar (sample1) to 10 bar (sample 2), and 15 bar (sample 4) led to decrease in cellulose dissolution time from 8 hours to 6 hours at 50^{o}C. This results shows that the pressure effects the dissolution of cellulose, and it provided a greater penetration of ionic liquid into cellulose and improved mass transfer. When the dissolving system was pressurized with high pressure (more than 1bar) the extreme condition was probably obtained. Thus the pressure effect provided excellent condition for cellulose dissolution in ionic liquid at lower temperature of the system.

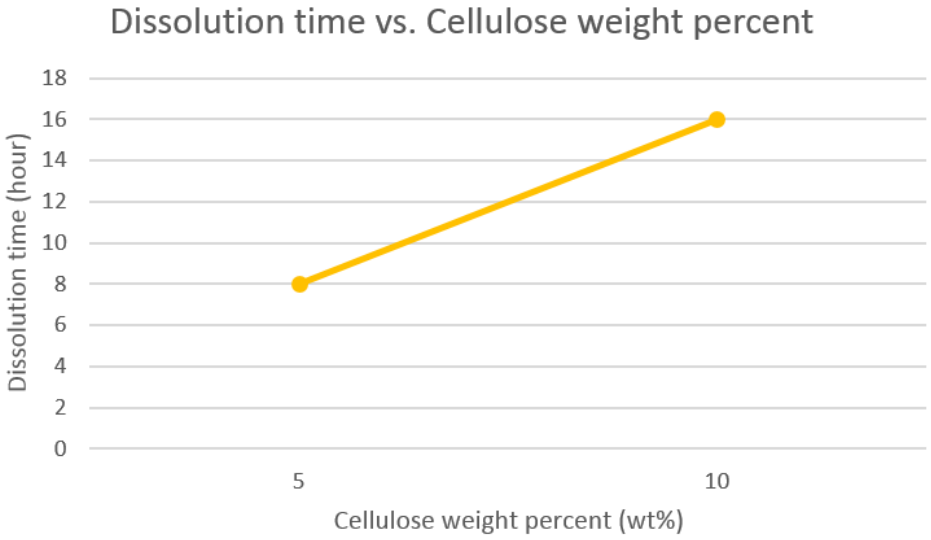
A graph was plotted to monitor the dissolution time behaviour respected to the pressurized time.

FIGURE 4.8. Graph on dissolution time vs pressure.



As shown on the graph above, we could observe that as the pressure is increased, the dissolution time is decreased. The experiment was conducted to collect and observed the trending as the pressure is increased up to 20 bar. Another graph was plotted to compare the dissolution time and the cellulose weight percent variation as shown in Figure 4.9

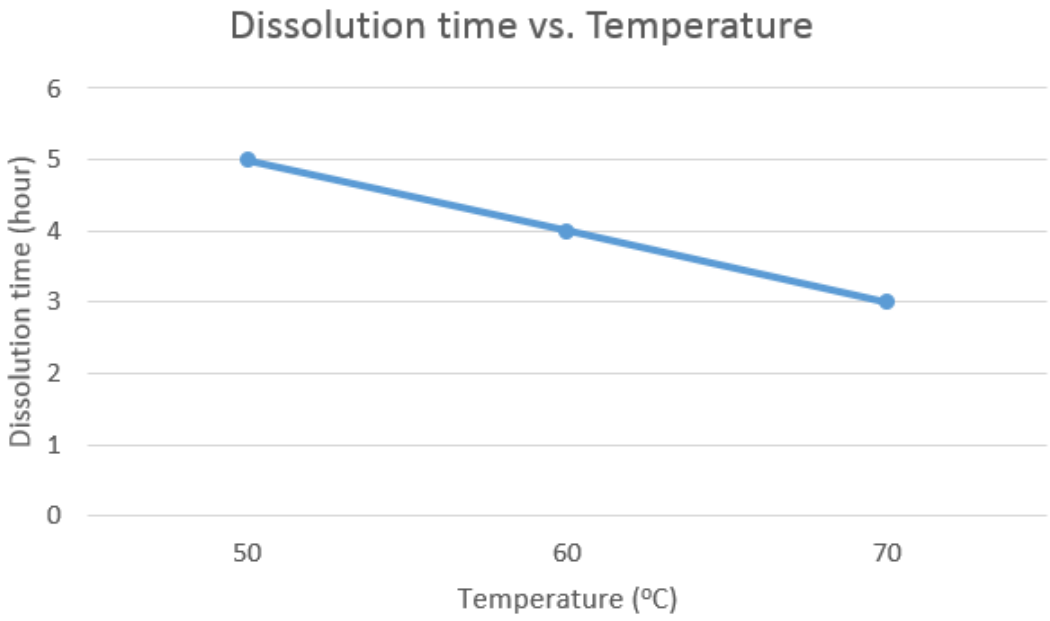
FIGURE 4.9. Graph on dissolution time vs cellulose weight percent.



As the weight percent of the cellulose is increased, the dissolution time is increased. The increment on the dissolution time is due to higher mass of cellulose presents in the mixture thus resulting a slower dissolution rate of cellulose in [EMIM][Ac].

To further advance the study, change in temperature with maintaining the pressure were conducted. The dissolution time was recorded as the temperature were rises from 50 – 70 ^{o}C. Graph below shows the data trending.

FIGURE 4.10. Graph on dissolution time vs temperature.

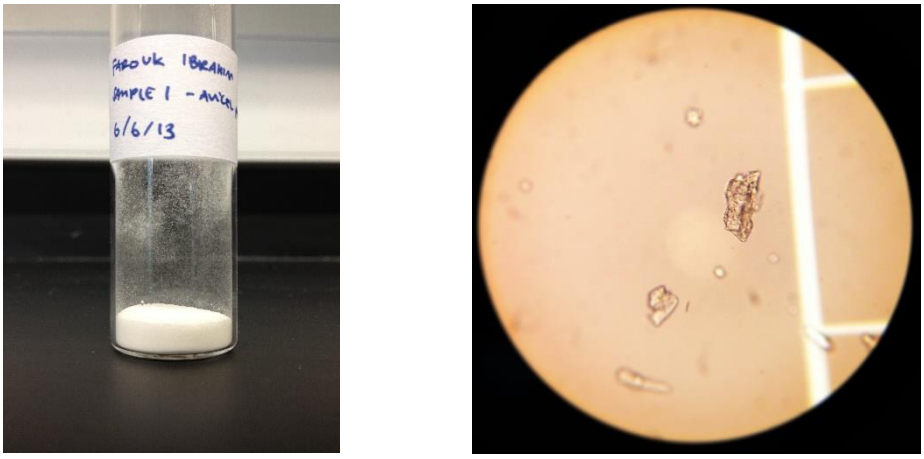


Based on the graph above, it shows that as the temperature is increased, the dissolution time is decreased. In Roger's research paper, it shows that the optimum dissolution of cellulose in ionic liquids is best at 110 ^{o}C. After we pressurized, it shows that the dissolution temperature is lowered resulting less heat and energy needed for dissolution of cellulose.

Throughout the experiment conducted, a conclusion had come to end where the pressure, temperature and cellulose wt% does effect the dissolution rate.

4.3 Prototype

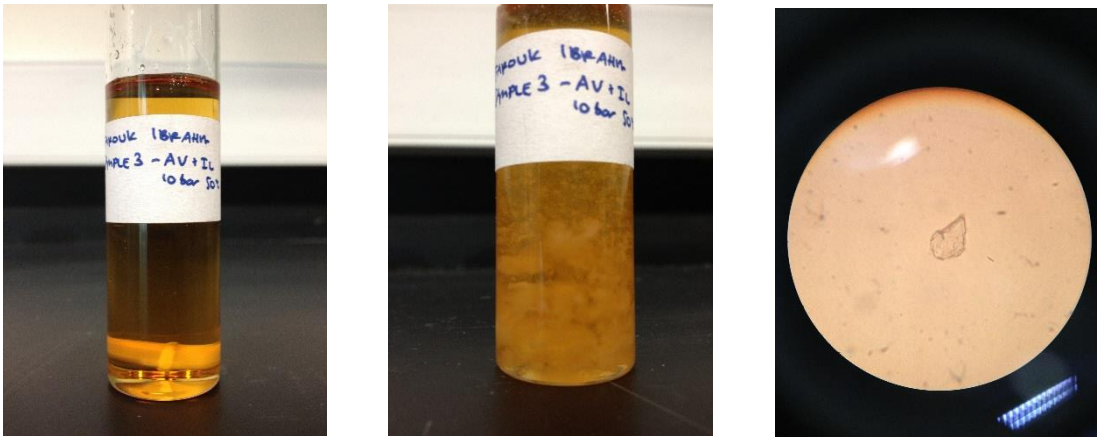
In this sub chapter, the sample prototype shall be discussed. Starting from the raw material up to the mixture of the materials when pressurized. Firstly, the cellulose that are being used is Avicel cellulose, which is the commercial cellulose available. Figure 4.11 shows the structure of the avicel cellulose.



(a) (b)

FIGURE 4.11. Avicel Cellulose in powder form (a) and micro structure of the avicel cellulose under microscope view (b).

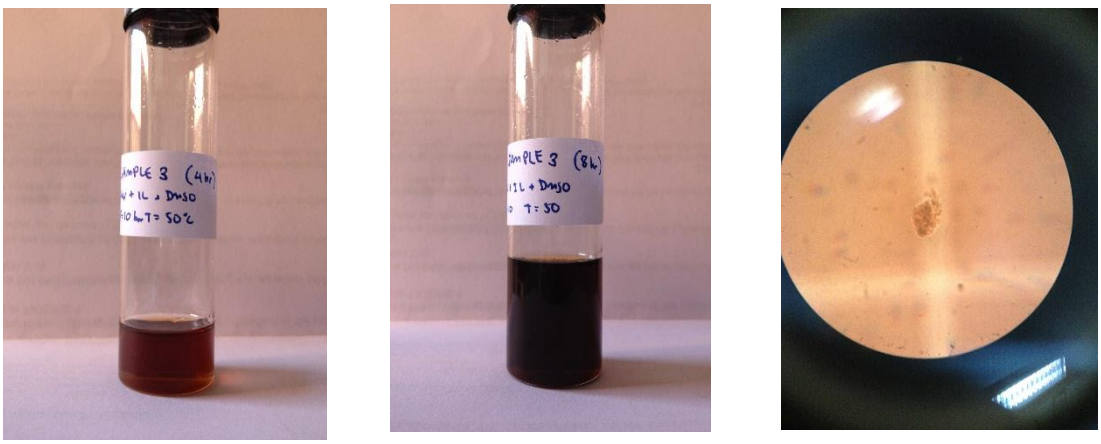
These avicel cellulose will be added into the mixture of ionic liquid ([EMIM][Ac] and Dimethyl Sulfoxide, DMSO) and let to dissolve in certain period of time. Figure 4.12 shows the initial sample of [EMIM][Ac] and DMSO before and after the addition of cellulose.



(a) **(b)** **(c)**

FIGURE 4.12. [EMIM][Ac] and DMSO before mixture (a) and after mixture with avicel cellulose (b). The micro-structure of avicel cellulose in the ionic liquid (c).

The figure above shows the sample before the pressure treatment using high pressure cell. The structure of the cellulose are still in the normal behaviour and shape. Figure 4.13 below shows the sample of pressurized solution.



(a) **(b)** **(c)**

FIGURE 4.13. The sample after pressurized at 50^{o}C and 10 bar for 4 hours (a) and 8 hours (b). The micro-structure of avicel cellulose after pressurized at 10bar for 4 hours (c).

Figure 4.13 shows the pressurized sample mixture, we could observe that the structure of the cellulose was deformed and become smaller in size. The effect of pressure did contributed an important factor in the dissolution of cellulose in ionic liquids.

CHAPTER 5 CONCLUSION

In conclusion, objective of this study is achieved, where pressure could effectively effects the dissolution of cellulose in ionic liquids. An increase of the pressure from 10 to 20 bar resulted in the decrease in cellulose dissolution time. The weight percent of the cellulose in the sample were also contributed to the dissolution time rate. The relation gives that the higher weight percent of cellulose, the longer it take to dissolve cellulose in the ionic liquid. The variation of temperature did effects the dissolution time as the temperature is increased, the dissolution time is decreased.

The sample were later analyzed by using a microscope to indicate the cellulose structure before and after pressure treatment. The micro structure of every sample collected were observed, analyzed and discussed.

A further work extension shall be conducted with different pressure set point and the dissolution rate for each experiments/runs shall be tabulated and analyzed. Other than that, the future expansion for this project is to replace the commercialized avicel cellulose with natural cellulose such empty fruit bunch (EFB) or dried woods. A different types of ionic liquids could be used to compare the dissolution rate.

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