STUDY ON DEGRADATIVE SOLVENT EXTRACTION OF BIOMASS AND COAL BY 1-METHYLNAPTHALENE, BIODIESEL AND WS3060 AT 350 °C

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A THESIS SUBMITTED AS A PART OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF ENGINEERING
IN ENERGY TECHNOLOGY AND MANAGEMENT

THE JOINT GRADUATE SCHOOL OF ENERGY AND ENVIRONMENT
AT KING MONGKUT’S UNIVERSITY OF TECHNOLOGY THONBURI

2ND SEMESTER 2013

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ABSTRACT

The degradative solvent extraction of biomasses including rice straw (RS) and Leucaena (LC) and coal was studied. This method treats raw material in solvent at around 350 ^{o}C, under pressure, to dewater, remove oxygen functional groups, and to produce low-molecular-weight compounds. The solvent acts as a dispersant for the sample and it does not participate in chemical reaction. In this study, 1-Methylnaphthalene (1-MN), Biodiesel from palm oil (B100) and WS3060 were used as a solvent. The products were separated into residue (termed “Residue”), gaseous products and the extract in solvent. The extract was recovered as a solid by removing the solvent by vacuum evaporator and was called “Soluble”. The small molecular compounds dissolving in the solvent were removed together with the solvent was called “Liquid”. The yield of “Liquid” could not be measured directly, but was calculated by the difference.

At 350 ^{o}C, the carbon-based yields of the Soluble fraction from RS and LC were as large as 57.2 % and 58.2 %, respectively when using 1-MN as a solvent. On the other hand, the highest yield of the Soluble fraction from coal was found at 380 °C and was 34.6 %. It is difficult to remove the solvent from the Soluble fraction when using B100 as a solvent due to its high boiling point. Therefore the “Soluble + Liquid” fraction for B100 was quantified by the difference. At 350 ^{o}C, the carbon-based yields of the “Soluble + Liquid” fraction from RS, LC and coal were as large as 43.5 %, 46.1 % and 17.0 %, respectively. The extraction yields were increased when increasing treatment temperature to 380 ^{o}C. The carbon-based yields of the “Soluble + Liquid” fraction from RS, LC and coal were as large as 45.3 %, 51.7 % and 17.7 %, respectively. The last solvent was WS3060. The carbon-based yields of the Soluble fraction from RS, LC and coal were 8.7 %, 10.5 % and 5.9 %, respectively when using this solvent. The Soluble yields extracted from this solvent were very small when compared with 1-MN solvent and B100. This is probably because the soluble product does not dissolve in WS3060 and precipitated into solid at room temperature. These results indicated that B100 and WS3060 had a potential as a solvent for the degradative solvent extraction.

Keywords: Biomass; Degradative Solvent Extraction;Upgrading

ACKNOWLEDGEMENTS

My valuable thesis would not have been successful without several people who kindly helped and supported this thesis. They have contributed and extended their invaluable assistance to the preparation and completion of the study. Firstly, I am really grateful to my supervisor, Assoc. Prof. Dr. Nakorn Worasuwannarak. He always answered my questions and he gave me many wonderful ideas. Sometime, when I fell in the hopeless he encouraged me for throughout the problem. I will remember his helpfulness. In addition, I would like to thank the financial support, chemicals support, and efficient laboratory for this research by the Joint Graduate School of Energy and Environment (JGSEE).

Finally, I would like to thank my family. Thank you for their love and encouragement whenever I had problems. Thank you my lovely family. Last of all, thank you my patience and mind to across every problem which contributed to my success.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont')

LIST OF FIGURES (Cont')

CHAPTER 1

INTRODUCTION

1.1 Rationale/Problem statement

Nowadays, coal is an important energy resource. It is used as a solid fuel in many industries such as power plants, cement plants and steelworks plants, etc. Coal is valuable resource, not only used as fuels but also as chemical feedstock. It has several advantages when considered as a feedstock for chemicals and carbon-based materials. The usage of coal in Thailand is mostly for power plant. The coal that used in Thailand is almost lignite which is the low rank coal and some imported coal such as sub-bituminous and bituminous. One of the problems of coal usage is small particles of coal, because the sizes are too small to use in the boiler. Therefore, it is necessary to utilize this coal more efficiently.

Biomass is also an abundant hydrocarbon resource. It is a renewable resource, because it can be re-grown, regenerated and recycled. In an agricultural country as Thailand where there are various biomass and agricultural residues. The biomass resources are currently used as a solid fuel to generate electricity and heat through combustion. To utilize the biomass more efficiently, there are many studies about conversion technologies to upgrade or produce more efficient fuel or valuable product. Nowadays the conversion technologies can be categorized into thermochemical such as pyrolysis, carbonization, gasification, hydrothermal liquefaction and organosolv method, and biochemical conversion such as enzymatic hydrolysis and fermentation. For example, pyrolysis is thermal decomposition in absence of oxygen condition which converts biomass to liquid (termed bio-oil or bio-crude), solid and gaseous products. In addition to the technologies mentioned above, degradative solvent extraction technique is the conversion process which can produce high quality carbonaceous materials and more valuable products than to be used as fuel.

Degradative solvent extraction has been studied for coal and more effectively applied in low-rank coal. This method has also been studied with biomass. The purpose of this method is to upgrade and fractionate feedstock organic compound. The method has many advantages such as producing low-molecular-weight compounds and fractionating the various samples at lower temperature. Furthermore the solvent can be recovered and reuse again. The method treats raw material in non-polar solvent at around 350 °C, under pressure. The solvent plays an important role in degradative solvent extraction. The concept of this method involves exposing the whole sample to thermal reaction in solvent at around 350 °C. The solvent does not participate in chemical reactions with the samples but to act as a dispersant for the sample [1]. The solvent often used in most of the studies involving this method is non-polar solvent such as tetralin or 1-methylnathalene. Wannapeera *et al.* used 1-methylnathalene (1-MN) as a solvent to extract various biomasses. It was found that 1-MN which is recovered and analyzed by GC-MS does not change. 1-Methylnaphthalene (1-MN) will be used as a solvent in this study. This work proposes to select other solvents available in Thailand to use for the degradative solvent extraction, because 1-methylnaphthalene is too expensive. Finding more practical solvent instead of 1-MN is very challenging. The solvent must not react with the biomass sample at 350 °C. Biodiesel from palm oil and WS3060 will be used as a solvent to meet this requirement.

1.2 Literature review

There are many works that study the degradative solvent extraction process, especially with coal. The degradative solvent extraction at below 350 °C is a high potential process use and has been widely studied. The purposes of this method are producing precursors of chemicals and carbon materials by dewatering and fractionation. The products from this method are three main products including residue (some author call upgrade coal), the solid extract that precipitated from the extract at room temperature (call "deposit") and the extract soluble in solvent even at room temperature (call "soluble"). Many studies report that gaseous product occurred by this method is mostly CO_2. Several studies have looked at the effect of experimental parameters on product distribution. The three principal parameters studied are temperature, solvent, and the nature of raw material: such as the rank of coal or biomass chemical composition. [2]

1.2.1 Thermal decomposition of low rank coal and biomass at about 350 °C

Pyrolysis is generally described as the thermal decomposition of the organic components in biomass. Figs. 1.1 (a) and (b) show the thermal decomposition of various low rank coals and various biomasses. At temperature about 350 °C, the weight loss of biomass is significant bigger than low rank coal. Biomass begins to produce tar which is low molecular weight liquid at about this temperature while coal start to produce tar at temperature above 400 °C. Worasuwannarak et al. studied the pyrolysis behaviors biomass by TG-MS technique. For example, the pyrolysis behavior of rice straw is shown in Figure 1.2. The weight of rice straw started to decrease at above 150 °C. At 350 °C, CO, CO$_2$, H2 and CH$_4$ are performed. Tar, which is a low molecular weight compound, and water are also performed at this temperature. The reactions occurring during the degradative solvent extraction are thought to be similar to those occurring during pyrolysis in an inert atmosphere. The major differences between the degradative solvent extraction and pyrolysis (Figure 1.2), the degradative solvent extraction can produce high low molecular weight compound at lower temperature in term soluble product. So the mechanism of degradative solvent extraction between coal and biomass are difference. [3]

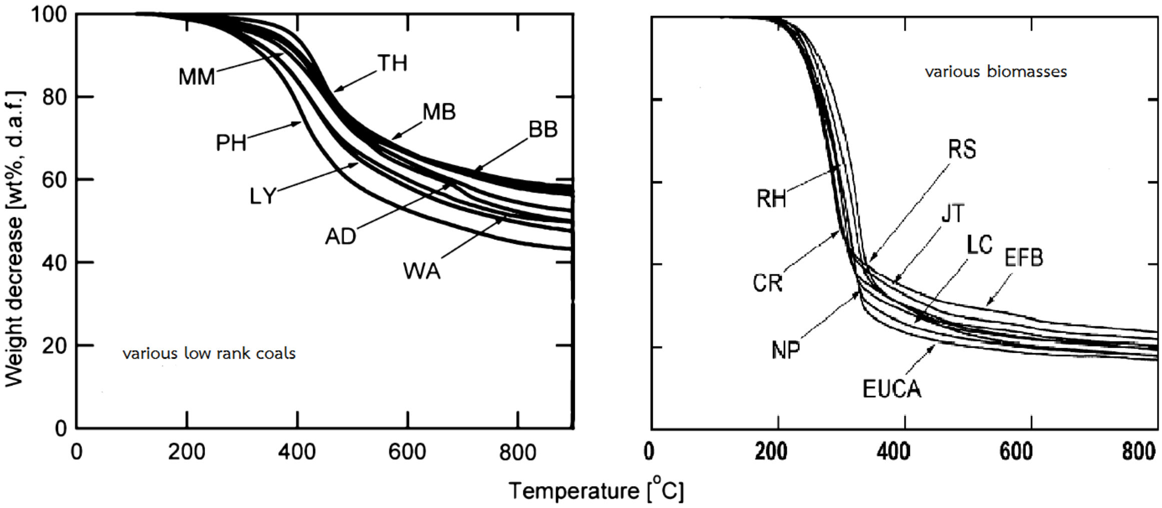


Figure 1.1 Thermal decomposition of various low rank coals (a) [4]
and various biomasses (b) [1]

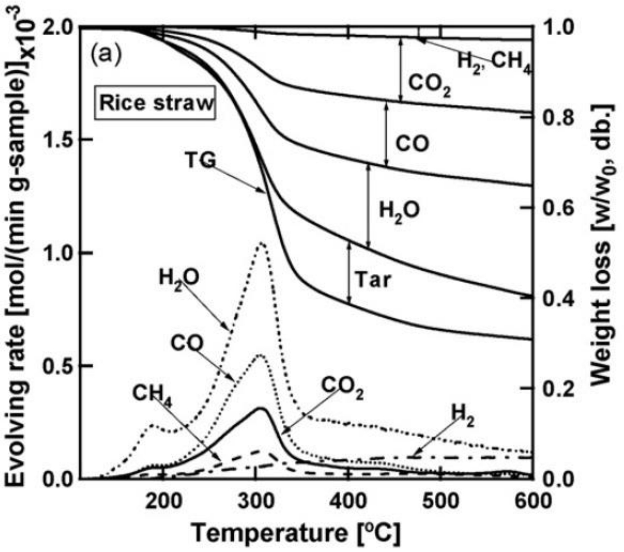


Figure 1.2 Thermal decomposition of rice straw [3]

1.2.2 Thermal behavior of degradative solvent extraction

K. Miura *et al.* studied the coal extraction in a flowing stream of solvents including tetralin and 1-methylnaphthalene. PITT and UF coals, which are the high rank coals, were used. The extraction temperature was raised linearly at the rate 10 °C/min. The yields of residue were plotted against the extraction temperature in Figure 1.3. From the results, yield of residues decreases when the temperature of extract increases. At 350 °C, the yield of residue reached to 70-75%, and little gaseous products were occurred at below this temperature. To compare with thermal decomposition by pyrolysis behavior, at 350 °C, the weight of two coals decreased only 3%.

The low rank coals, MW (Morwell coal), HPO60.2 and HPO60.24 were also studied. For extract yields which presented by residue yield had the tendency similar to high rank coal. A Large amount of gaseous components were formed at temperature above 300 °C because the low rank coal starts to decompose at lower temperature. The residue yields, however, were significantly smaller than weight loss by thermal decomposition. The results indicate that the low rank coal can be extracted to a certain extent at around 350 °C.

These results show that the thermal behavior of degradative solvent extraction differs to thermal decomposition in the gas phase pyrolysis. Coal samples start to degrade at temperatures below 350 °C in the solvent. It can be concluded that the small molecule of coals can be extracted at temperature below 350 °C in solvent condition. Moreover the coal rank also affects in thermal behavior of degradative solvent extraction. [5]

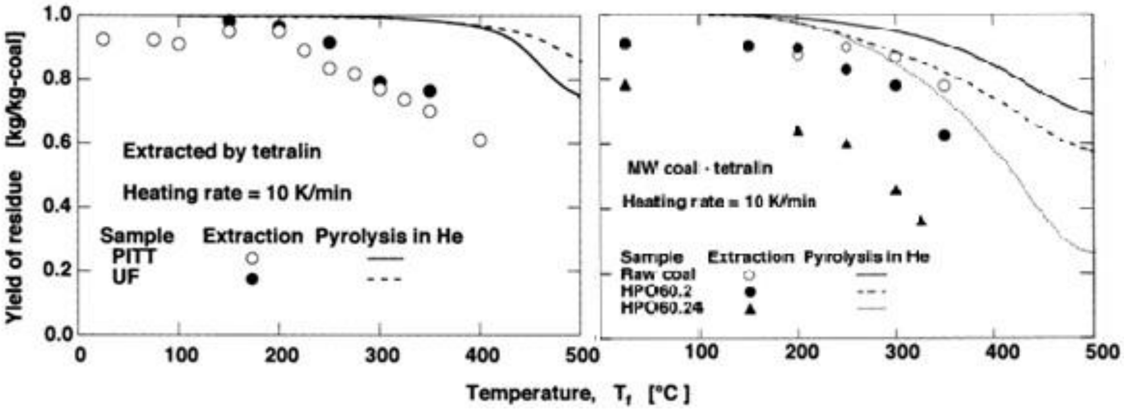


Figure 1.3 Change in the residue yield with the increase of extraction/depolymerization temperature for (a) High rank coals and (b) Low rank coals [5]

1.2.3 Degradative solvent extraction of coal

Li *et al.* studied the production of degradative solvent extraction by using eight kinds of low-rank coals including lignites and sub-bituminous coals. The coals included lignites from Thailand and the Philippines, brown coals from Indonesia, Australia and Malaysia, and two sub-bituminous coals from Indonesia. The ultimate and proximate analysis of coals and products were shown in the Table 1.1. This experimental was subjected in a batch reactor (autoclave) at 350 °C by using 1-methylnapthalene which is the non hydrogen donor as a solvent. The product yields was shown in Figure 1.4, the yields of solid product were 16.9-27.2 wt%, 3.5-16.9 wt% and 49.7-63.6 wt% on dry and ash free basis for soluble, deposits and residue respectively. The gaseous product was generated about 2.8- 8.7 wt % which mainly was CO_2 which is common in low rank coal. The liquid yields which consisted mainly of water reached to 10.6 wt% on dry and ash free basis that relate to carbon content of the raw coals. The results were showed that 21.8-40.7 wt% of selected coals can be extracted and more than 94.4% of carbon was recovered as solid fractions. Both the Solubles and Deposits were free from water and ash. Elemental compositions of Solubles were C = 81.8−84.8 wt %, H = 7.5−8.1 wt %, and O = 6.5−10.2 wt %. The carbon content of the Solubles was very high which were rather close to the elemental composition of bituminous coal. Moreover the Soluble and Deposit products which were extracted from low rank coal were completely free from water, and almost completely free from ash. [4]

Table 1.1 Ultimate and Proximate Analysis of Three Solid Fractions and Raw Coal

	ultimate analysis [wt %, d.a.f.]				**proximate analysis [wt%,d.b.]**		
	C	**H**	**N**	**O[diff.]**	**VM**[a]	**FC**[b]	**ash**
MM	66.4	3.9	1.9	27.8	50.2	24.0	25.8
soluble	82.4	7.4	2.3	7.8	78.5	21.3	0.2
deposit	76.4	5.1	3.8	14.7	39.3	59.3	1.4
residue	68.8	3.8	3.4	24.0	27.1	34.4	38.5
LY	66.7	4.7	0.9	27.7	51.5	47.0	1.5
soluble	81.8	7.5	0.5	10.2	83.4	16.3	0.3
deposit	77.5	5.0	1.0	16.9	39.4	59.9	0.7
residue	77.4	4.0	1.0	17.6	31.8	66.0	2.3
WA	67.1	5.1	1.0	26.9	50.5	47.9	1.5
soluble	81.9	7.8	1.0	9.2	85.6	17.4	0.0
deposit	75.6	5.7	1.4	17.9	43.4	55.9	0.7
residue	77.2	3.8	1.6	17.4	32.1	65.0	2.9
BB	71.0	4.9	1.3	22.8	43.4	52.5	4.1
soluble	82.3	7.8	1.1	8.8	80.6	18.5	0.9
deposit	77.2	5.5	1.9	15.3	47.1	51.9	1.0
residue	77.2	4.0	1.7	17.2	29.8	64.3	6.0
MB	71.7	4.8	1.7	21.9	42.8	52.6	4.6
soluble	82.4	7.6	1.8	8.2	81.5	18.1	0.4
deposit	76.4	5.7	4.2	13.7	47.4	52.1	0.4
residue	78.0	4.2	2.0	15.8	29.4	64.7	5.9
PH	72.2	4.6	0.9	22.3	51.5	36.7	11.8
soluble	82.9	8.1	0.9	8.1	85.5	14.1	0.4
deposit	78.1	5.4	1.9	14.6	38.7	60.4	0.8
residue	75.1	4.2	1.2	19.5	27.8	49.3	22.9
AD	72.9	5.1	1.0	21.0	51.7	46.5	1.8
soluble	81.8	7.7	0.7	9.8	79.0	20.6	0.4
deposit	76.9	5.6	1.2	16.3	53.7	45.6	0.7
residue	76.4	4.1	1.3	18.2	32.1	64.3	3.6
TH	80.7	5.0	2.0	12.3	41.6	50.2	8.2

	ultimate analysis [wt %, d.a.f.]				proximate analysis [wt%,d.b.]		
	C	H	N	O[diff.]	VM[a]	FC[b]	ash
soluble	84.8	7.7	1.1	6.5	77.2	21.7	1.1
deposit	80.0	5.6	2.0	12.4	45.2	53.6	1.2
residue	79.4	4.8	2.3	13.6	29.3	61.3	9.4

[a]Volatile matter [b]Fixed carbon

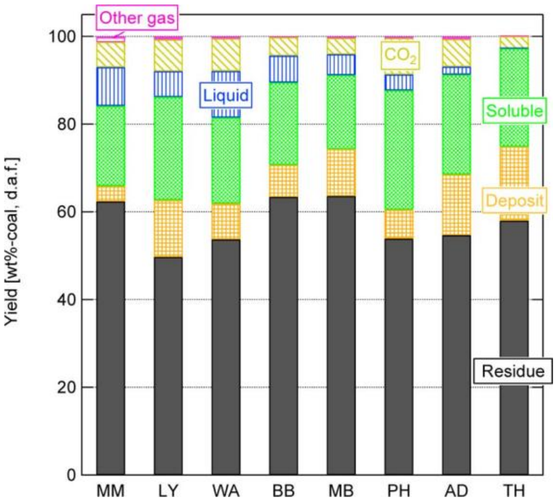


Figure 1.4 Product yields obtained by degradative solvent extraction. [5]

1.2.4 Degradative solvent extraction of biomass

Wannapeera *et al.* studied the production of degradative solvent extraction method by using 8 biomasses, namely Leucaena (abbreviated to LC), eucalyptus (EUCA), oil palm empty fruit bunches (EFB), jatropha trunk (JT) and cassava rhizome (CR), rice husk (RH), napier grass (NP) and rice straw (RS). In addition to the eight types of biomass, a microcrystalline cellulose, a hemicelluloses and a lignin were also collected. This experiment was subjected in a batch reactor (autoclave) at 350 °C by using 1-methylnapthalene as a solvent. The product yields, Ultimate and Proximate Analyses were shown in Table 1.2. For solid product, the carbon-based yield of Solubles, Deposites and Residues were 36.8-71.6%, 4.4-10.6% and 15.1-27.5% respectively. The element distributions of product are showed in Figure 1.5. The elemental compositions of the Solubles from the various biomasses were C = 81.0−83.3 wt %, H = 6.1−7.3 wt %, and O = 7.3−11.1 wt %. It was found that, the Soluble fractions which were extracted from various biomass contained the highest carbon. The oxygen about 82.5-88.4% was present in gaseous and Liquid fraction. This means that more than 80% of structural oxygen was removed as CO_2, CO and H_2O at 350 °C. Furthermore, most of the ash was concentrated in the Residues, whereas the Solubles were completely free from ash. [1]

Table 1.2 Product Yields, Ultimate and Proximate Analyses of various biomasses

Sample	Yield [wt%,daf]	ultimate analysis [wt %, daf]				proximate analysis [wt %, db]		
		C	H	N	O*	VM	FC	ash
CEL		41.2	6.1	0.3	52.4	92.4	7.6	0.0
Residue	4.1	79.5	4.3	0.7	15.5	36.6	63.4	0.0
Deposit	4.9	64.6	5.4	0.4	29.6	61.6	38.4	0.0
Soluble	28.3	84.9	6.1	0.5	8.5	73.3	26.7	0.0
HEM		45.7	6.8	0.3	47.2	78.3	20.3	1.4
Residue	13.4	70.0	5.5	0.3	24.2	64.3	35.7	0.0
Deposit	3.3	84.2	5.9	0.4	9.5	35.9	64.1	0.0
Soluble	24.5	84.0	6.7	0.4	8.9	65.4	34.6	0.0
LN		60.3	4.9	0.3	34.5	66.1	20.6	13.3
Residue	49.0	76.0	4.1	0.4	19.5	36.6	42.0	21.3
Deposit	1.5	77.9	4.6	0.6	16.9	40.8	59.2	0.0
Soluble	20.7	83.3	6.4	0.4	9.9	81.0	19.0	0.0
LC		49.3	6.6	1.4	42.7	82.1	16.6	1.3
Residue	12.3	86.4	5.3	1.9	6.4	35.7	54.9	9.4
Deposit	3.8	76.5	5.5	2.6	15.4	32.5	66.1	1.4
Soluble	36.9	81.5	6.4	2.2	9.9	75.5	24.5	0.0
EUCA		50.8	6.8	0.5	41.9	83.5	16.0	0.5
Residue	8.8	87.2	5.3	1.4	6.1	31.2	64.0	4.8
Deposit	5.2	80.1	5.5	1.5	12.9	39.8	59.8	0.4
Soluble	45.0	81.0	6.1	1.8	11.1	76.9	23.1	0.0
EFB		49.8	6.6	1.6	42.0	67.9	16.7	15.4
Residue	20.4	65.8	5.6	1.8	26.8	27.6	32.0	40.4
Deposit	3.0	89.5	6.2	3.2	1.1	32.9	65.9	1.2
Soluble	24.3	83.3	7.2	2.2	7.3	70.5	29.5	0.0
RS		46.2	6.7	1.6	45.5	73.0	11.9	15.1

Sample	Yield [wt%,daf]	ultimate analysis [wt %, daf]				proximate analysis [wt %, db]		
		C	H	N	O*	VM	FC	ash
Residue	14.6	61.7	5.0	1.7	31.6	24.0	22.8	53.2
Deposit	2.3	87.5	6.2	2.9	3.4	32.1	65.8	2.1
Soluble	31.5	82.3	6.8	2.0	8.9	74.8	24.4	0.8
RH		47.6	6.8	1.4	44.2	67.0	11.5	21.5
Residue	11.9	74.8	5.3	2.1	17.8	10.3	19.3	70.4
Deposit	6.4	87.0	5.9	2.7	4.4	37.7	62.1	0.2
Soluble	31.4	81.8	6.7	1.8	9.7	73.5	26.5	0.0
NP		50.8	6.8	0.5	41.9	76.0	16.7	7.3
Residue	17.4	87.2	5.3	1.4	6.1	32.7	36.7	30.6
Deposit	3.8	80.1	5.5	1.5	12.9	34.7	64.9	0.4
Soluble	21.3	81.0	6.1	1.8	11.1	69.0	30.0	1.0
JT		50.6	6.9	1.4	41.1	74.4	18.7	6.9
Residue	19.0	73.1	6.3	1.5	19.1	35.8	38.1	26.1
Deposit	3.0	89.1	6.5	3.1	1.3	34.7	63.7	1.6
Soluble	23.6	82.5	7.3	2.1	8.1	76.8	22.2	1.0
CR		49.4	6.9	1.4	42.3	75.9	17.8	6.3
Residue	17.3	77.2	5.7	1.7	15.4	31.6	43.0	25.4
Deposit	3.3	87.8	6.2	3.1	2.9	34.3	64.4	1.3
Soluble	25.4	82.0	6.9	2.0	9.1	75.9	24.1	0.0

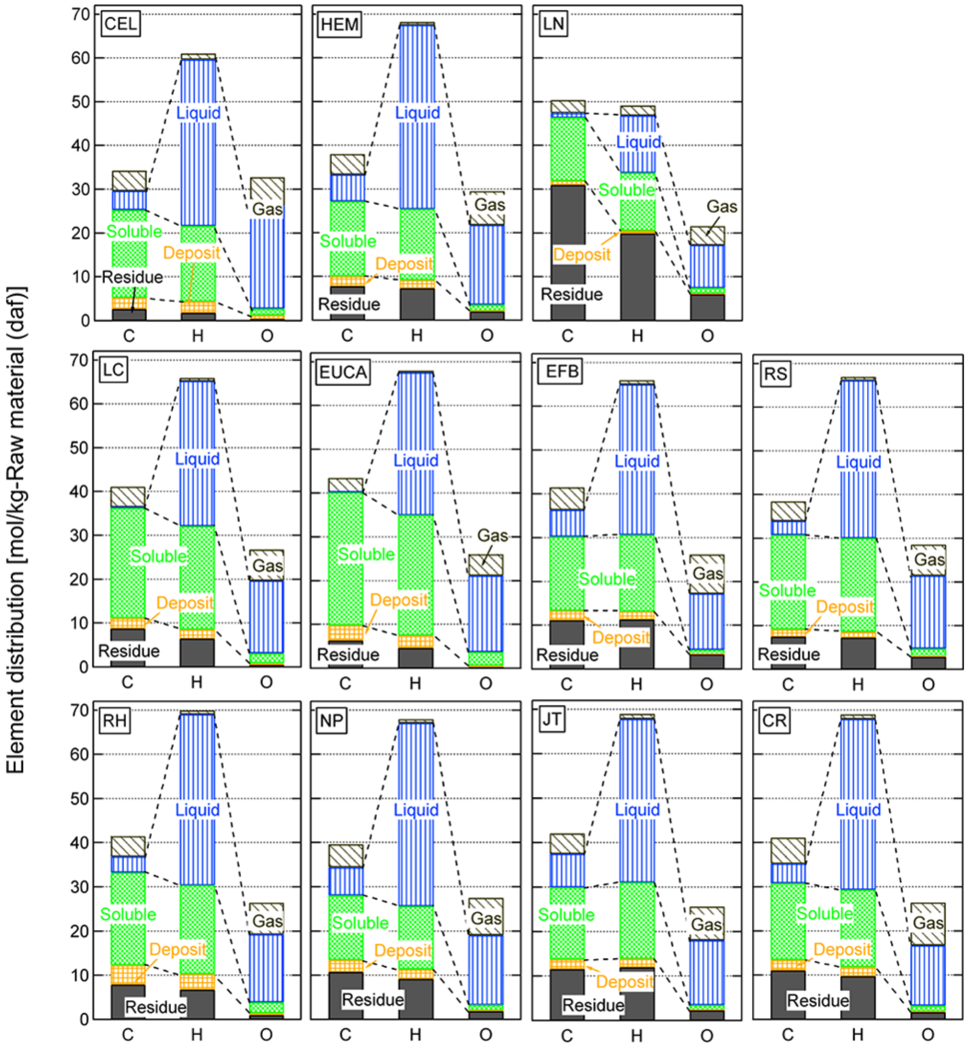


Figure 1.5 Element distribution in the products obtained by solvent treatment of all biomass samples at 350 °C. [1]

1.2.5 The role of solvent in degradative solvent extraction and its property

The solvent plays a very important role in degradative solvent extraction. The core concept underlying this method involves exposing the entire sample to thermal reactions in a solvent at around 350 °C. This method requires the solvent which not participate in chemical reaction with sample. The solvents which are mostly used for this method is a nonpolar solvent such as tetralin and 1-Methylnaphthalene (1-MN). 1-MN is very effective in degradative solvent extraction of both coal and biomass. 1-MN is derived from coal tar. 1-MN is well known as a hydrogen donor solvent, so this solvent does not reactive with sample.

Wannapeera *et al.* extracted various biomasses using 1-MN as a solvent. The authors proposed the role of 1-MN in degradative solvent extraction by analyzing the 1-

MN which was recovered after treatment by GC-MS. It was found that only 1-MN and water were detected. It shows that the 1-MN was not significantly altered during the solvent treatment [1].

Two solvents, including tetralin and 1-methylnaphthalene, were compared for coal extraction by K. Miura *et al.* PITT which is the high rank coal was used. The tetralin is well known as a hydrogen donor solvent, its hydrogen donor ability may have effect on extraction yield. From the result is showed in Figure 1.6, about 70% of PITT coal can be extracted at 350 ^{o}C by using both tetralin and 1-methylnapthalene. It was found that using both tetralin and 1-MN gave almost the same extraction yields over the whole extraction time. This indicated that hydrogen donor ability of tetralin does not affect the extraction below 350 ^{o}C. Therefore the solvent that stable at temperature around 350 ^{o}C can be used for degradative solvent extraction. [5]

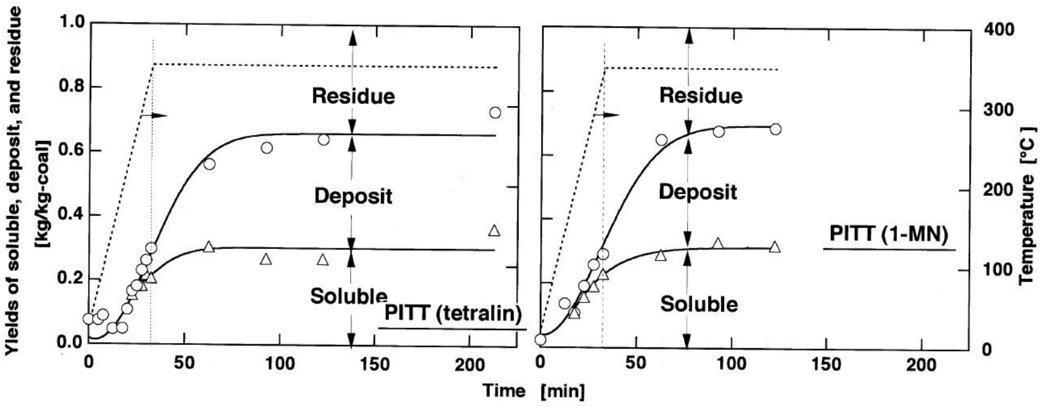


Figure 1.6 Change in the yield of soluble, deposit and residue with the increase of the holding time at 350 °C for PITT coal [5]

K. Miura *et al.* presented the solvent extraction method for extracting coal. Twenty coals were extracted by tetralin and two coal derived oil (carbol oil and creosote oil) at 350 ^{o}C. The total extraction yields were defined as the sum of the yields of deposit and soluble. Figure 1.7 (a) shows the yield product of twenty coal extracted by tetralin. UF coals reached to 82% for the product yield. The extraction yields exceeded 60% for IL, Mi, Eb, ES and PITT. Using tetralin as solvent is effective to extract some sub-bituminous and bituminous coal. Carbol oil which is a high polar solvent was also used for extract twenty coals which shown in Fig. 1.7(b). The extraction yields for lower rank coals were very high such as MW which was the lowest rank coal (its carbon contain only 67.1%) in this study.

Its extraction yield high about 70%. Thus, it was showed that carbol oil is effective for extract lower rank coal. Eight coals were extracted (showed in Fig. 1.7(c)) by creosote oil. The extraction yields which extracted by this solvent were close to those in tetralin, but all of the extract were soluble. Polar compounds in the creosote oil were judged to contribute to dissociation of the aggregated structure of the fraction corresponding to the deposit obtained in tetralin.

To study the mechanism of the extraction in the carbol oil, a bituminous coal PITT and brown coal MW were chosen as the coal samples and mixed solvents, tetralin/cresol (7/3), tetralin/cresol/naphthalene (5.8/2.5/1.7) and tetralin/phenol (10/1) were also used as a model solvent to examine the extraction behaviors by coal-derived oil. Comparing the extraction yields obtained from the mixed solvents, tetralin/cresol and tetralin/cresol/ naphthalene, with those obtained using tatralin, the carbol oil, and the creosote oil for PITT. Figure 1.8 shows that the amount of deposit decreased significantly by adding cresol to tetralin, and it was null for carbol oil and the creosote extractions. This means that the polar components in solvent contributed to dissociate the aggregated structure of the components corresponding to the deposit fraction for the tetralin extractions.

For brown coal (MW) extraction, tetralin, tetralin/phenol and carbol oil were used as model solvents. The degree of polarity decreases from carbol oil to tetralin. The results are shown in Figure 1.9. The extraction yield increased and the amount of gaseous products decreased when the polarity of solvent increased. It means that the polarity of solvent affected the extraction of low rank coal. The yield of gaseous product decreased, it indicated that the decomposition of brown coal is suppressed by using polar solvent. [6]

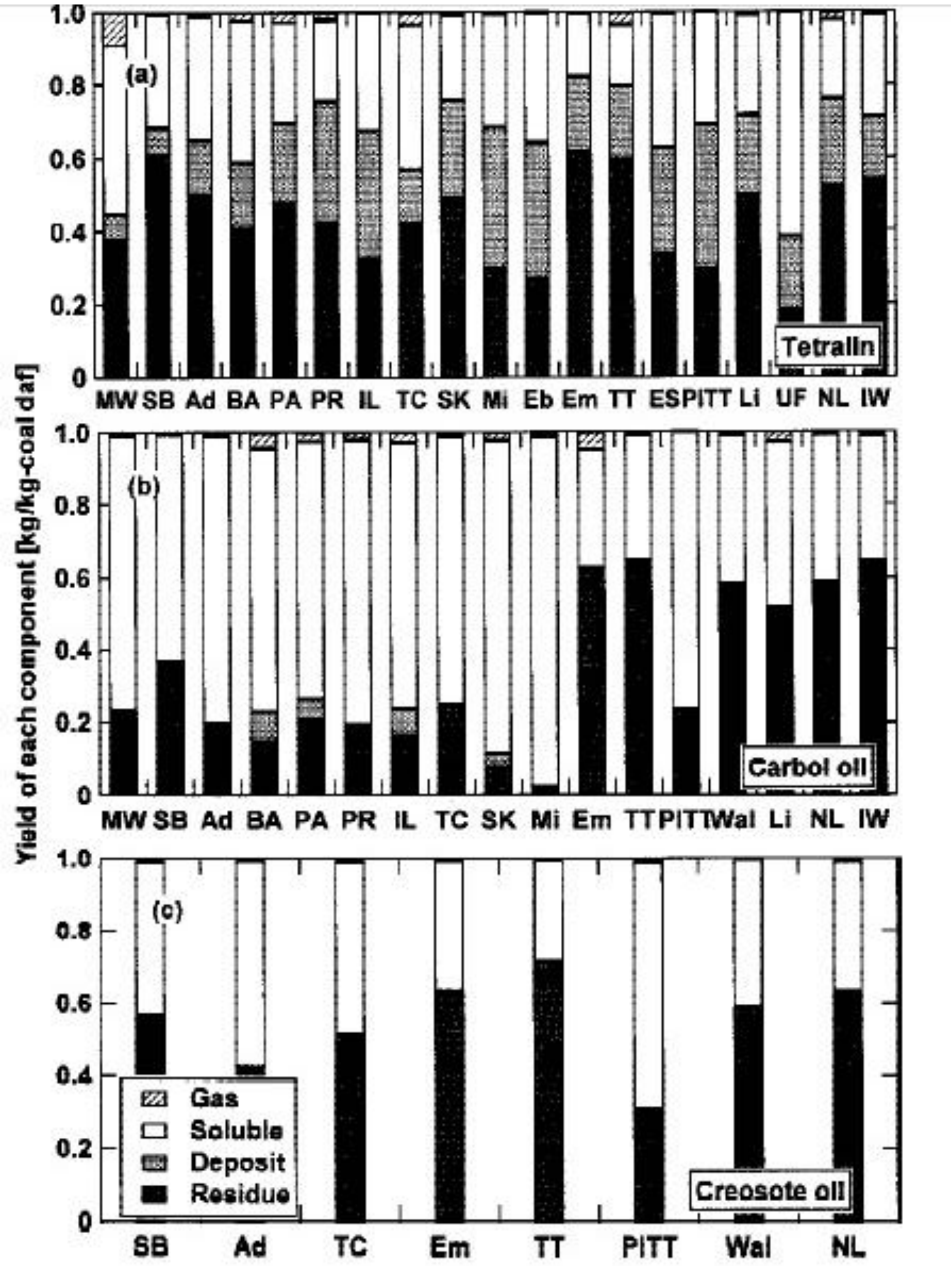


Figure 1.7 Yields of gaseous product, soluble, deposit and residue for various coals through the extraction using (a) tetralin, (b) carbol oil, and (c) creosote oil at 350 °C. [6]

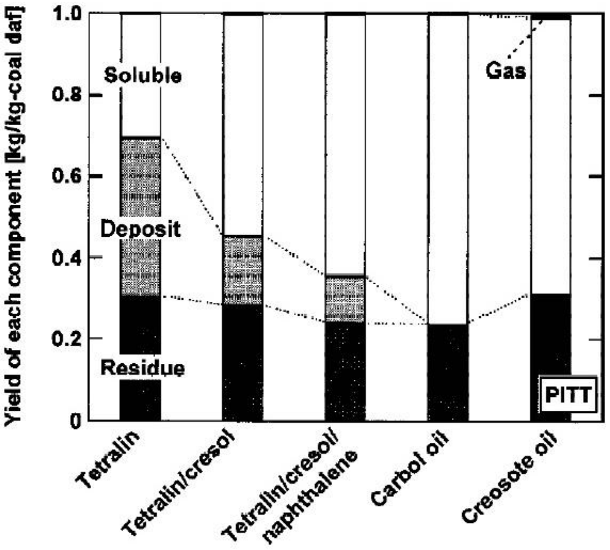


Figure 1.8 Yields of gaseous product, soluble, deposit and residue for PITT through the extraction using various solvents at 350 °C. [6]

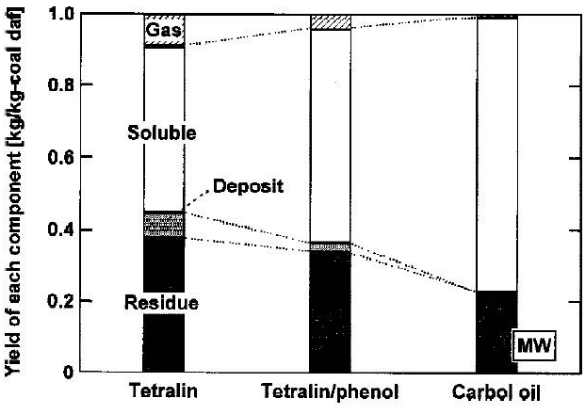


Figure 1.9 Yields of gaseous product, soluble, deposit and residue for MW through the extraction using various solvents at 350 °C. [6]

1.2.6 The effect of the solvent-treatment temperature

Wannapeera *et al.* studied the effects of the solvent-treatment temperature on the product yield was examined at 250, 300, and 350 °C using EFB and RS. Table 1.3 gave the weight basis yields of the products, the elemental compositions of the solid products, and the element distributions of carbon, hydrogen, and oxygen in the products of EFB and RS.

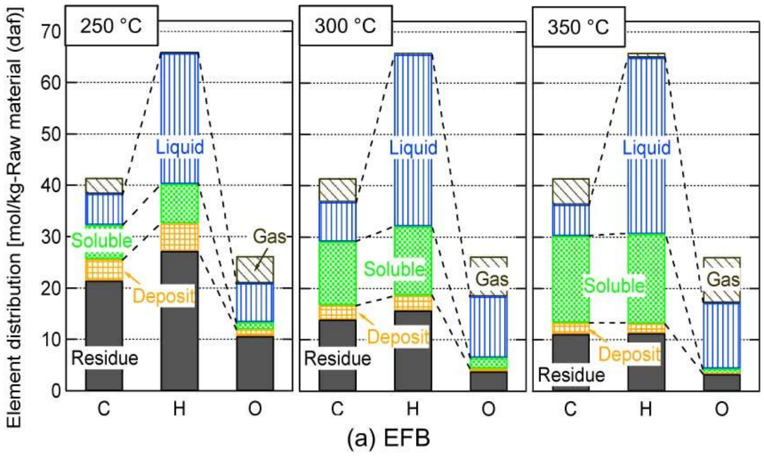
The results showed that increasing the solvent-treatment temperature, the Solubles from EFB and Rs will increase. Figure 1.10 showed the effect of solvent treatment temperature on the element distribution in the product for (a) EFB and for (b) RS. For the EFB, at 350 °C, oxygen distribution about 82.5% contained the gaseous product or the

Liquid. These results indicated that more than 80% of the oxygen in the samples was removed as CO_2, CO, and H2O at 350 °C. The carbon from EFB was distributed to the Soluble, Deposit, and Residue fractions at about 40.7%, 5.3%, and 27.0% respectively, indicating that 73.0% of the carbon was retained in the solid product. The similar trend in the case of rice straw, 350 °C, oxygen distribution about 83.8% contained the gaseous product or the Liquid. The carbon about 80.0% from RS was retained in the solid product. From these results, the oxygen distribution in the gaseous product and Liquid increased when increasing treatment temperature for both EFB and RS and more than 80% of the oxygen in the samples was removed as CO_2, CO, and H2O at 350 °C. The loss of carbon to gaseous products was mainly due to the formation of CO_2. These results indicated that the thermal reactions are deoxygenation reactions involving dehydration and decarboxylation. It clearly show that the proposed solvent treatment at 350 °C is very effective for simultaneous deoxygenation and recovery of a solid product having a high carbon content and low oxygen content in rather high yield from both EFB and RS. [1]

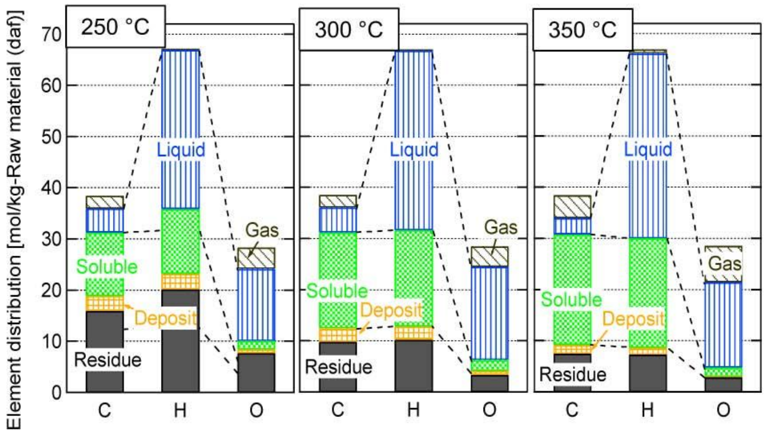
Table 1.3 Product Yields, Ultimate and Proximate Analyses of various biomasses and different temperatures

Sample	Yield [wt%,daf]	Ultimate analysis [wt %, daf]				Elemental balance [mol/kg-biomass, daf]		
		C	H	N	O*	C	H	O
EFB		49.8	6.6	1.6	42.0	41.5	66.0	26.3
Treated at 250°C								
Residue	46.2	55.8	5.9	1.3	37.0	21.5	27.3	10.7
Deposit	7.8	64.5	6.7	1.7	27.1	4.2	5.3	1.3
Soluble	11.2	71.5	6.9	2.0	19.6	6.6	7.7	1.4
Gas	12.2					3.1	0.2	5.3
Liquid	22.3					6.1	25.5	7.6
Treated at 300°C								
Residue	25.1	67.2	6.3	1.7	24.8	14.0	15.8	3.9
Deposit	4.8	71.0	6.1	2.3	20.6	2.8	2.9	0.6
Soluble	19.9	74.9	6.8	1.8	16.5	12.4	13.5	2.1
Gas	18.1					4.6	0.4	7.8
Liquid	31.7					7.7	33.4	11.9

Sample	Yield [wt%,daf]	Ultimate analysis [wt %, daf]				Elemental balance [mol/kg-biomass, daf]		
		C	H	N	O*	C	H	O
Treated at 350°C								
Residue	20.4	65.8	5.6	1.8	26.8	11.2	11.4	3.4
Deposit	3.0	89.5	6.2	3.2	1.1	2.2	1.8	0.0
Soluble	24.3	83.3	7.2	2.2	7.3	16.9	17.5	1.1
Gas	20.6					5.1	1.0	8.9
Liquid	31.7					6.1	34.3	12.8
RS		46.2	6.7	1.6	45.5	38.5	67.0	28.4
Treated at 250°C								
Residue	34.3	56.2	5.9	1.8	36.0	16.0	20.2	7.7
Deposit	5.2	67.1	5.7	2.4	24.8	2.9	3.0	0.8
Soluble	19.2	77.2	6.6	2.5	13.7	12.4	12.7	1.6
Gas	9.8					2.5	0.1	4.2
Liquid	31.3					4.7	31.0	14.1
Treated at 300°C								
Residue	18.5	63.2	5.5	2.2	29.0	9.8	10.2	3.4
Deposit	4.6	69.2	5.9	2.4	22.5	2.7	2.7	0.7
Soluble	28.5	78.7	6.6	2.2	12.5	18.7	18.8	2.2
Gas	9.5					2.5	0.2	4.0
Liquid	38.6					4.9	35.1	18.2
Treated at 350°C								
Residue	14.6	61.7	5.0	1.7	31.6	7.5	7.3	2.9
Deposit	2.3	87.5	6.2	2.9	3.4	1.7	1.4	0.1
Soluble	31.5	82.3	6.8	2.0	8.9	21.6	21.4	1.8
Gas	17.0					4.5	0.8	7.1
Liquid	34.0					3.2	36.1	16.7



(a) EFB



(b) RS

Figure 1.10 Effect of solvent treatment temperature on the element distribution in the product for (a) EFB and for (b) RS [1]

1.3 Objectives

1) To study the possibility of using biodiesel from palm oil (B100) and WS3060 solvent to replace 1-Methylnaphthalene in degradative solvent extraction.

2) To study the extraction efficiency of biomass and coal with three solvents: 1-Methylnaphthalene, biodiesel from palm oil (B100) and WS3060 by degradative solvent extraction.

1.4 Scopes of research work

Degradative solvent extraction was performed at temperatures below 350 ^{o}C and under pressure for this thesis work. This study uses one coal sample and two biomass samples. The coal sample is coal from PTT Co. Ltd. The two biomass samples are Luecaena collected from Saraburi province and rice straw collected from Chiang Mai province. The coal and biomass samples were subjected to a degradative solvent extraction method, which treats the sample in a solvent under pressure at around 350 ^{o}C. 1-Methylnaphthalene (1-MN) was used as a solvent in this study. In addition to 1-MN, the biodiesel from palm oil and WS3060 was used as a solvent in this study.

The detail research work scope cover

1.4.1 Raw sample analysis

A. Chemical properties analyses and calorific value calculations

B. Chemical composition analyses

1.4.2 Degradative solvent extraction experiments of coal and biomasses were performed using 400 mg of each sample in 8 ml of each solvent (3 types). Each sample was then heated to 350 ^{o}C and held for 1 hr.

1.4.3 Blank test experiments for all 3 solvents were achieved under the same procedure as the above experiment.

1.4.4 The yield of products which were divided into 3 fractions as Soluble, Residue and gaseous product, were measured by weighing method.

A. Extract product, which is the soluble fraction (main product) in the solvent, was concentrated by removing the solvent using rotary vacuum evaporator at 170-190 ^{o}C and then dried in vacuum oven at 170-190 ^{o}C.

B. Residue that remains in the reactor was dried in vacuum oven at 170 ^{o}C.

C. The gaseous products were collected in a gas bag and analyzed by Gas Chromatography.

1.4.5 Characterization of the Soluble and Residue

A. Ultimate analysis (CHN)

B. Proximate analysis (TGA)

C. Thermogravimetric (TG) curve (under nitrogen atmosphere at a heating rate of 10 ^{o}C/min

D. Heating value (Bomb calorimeter)

E. Functional group (FTIR)

CHAPTER 2

THEORIES

2.1 Coal

Coal is a well-known substance and an important natural resource. It is also a complex and diverse material. It is the one of fossil fuels which is the most important readily available energy resource and reserves. Coal consists of a complex mixture of organic chemical substances containing carbon, hydrogen and oxygen, together with smaller amounts of nitrogen, sulphur and some trace elements, and the example for chemical structure is showed in Figure 2.1. Coal is a fossil or an organic sedimentary rock that formed by the action of temperature and pressure on plant debris and always has associated with it various amounts of moisture and minerals. Coal which is the combustible black or brownish-black organic sedimentary rock usually occur in rock strata in layers or veins called coal beds or coal seams. The harder forms, such as anthracite coal, can be regarded as metamorphic rock because of later exposure to elevated temperature and pressure. Coal has been used as resource for a long time. It is primarily burned for the production of electricity and/or heat, and is also used for industrial purposes, such as refining metals. [7]

2.1.1 Types of coal

Coal forms when dead plant matter is converted into peat, which in turn is converted into lignite, then sub-bituminous coal, after that bituminous coal, and lastly, anthracite. This involves biological and geological processes that take place over a long period. As geological processes apply pressure to dead biotic material over time, under suitable conditions it is transformed successively into:

Peat, considered to be a precursor of coal, has industrial importance as a fuel in some regions, for example, Ireland and Finland. In its dehydrated form, peat is a highly effective absorbent for fuel and oil spills on land and water. It is also used as a conditioner for soil to make it more able to retain and slowly release water.

Lignite, or brown coal, is the lowest rank of coal and used almost exclusively as fuel for electrical power generation. Jet, a compact form of lignite, is sometimes polished and has been used as an ornamental stone since the Upper Palaeolithic.

Sub-bituminous coal, whose properties range from those of lignite to those of bituminous coal, is used primarily as fuel for steam-electric power generation and is an important source of light aromatic hydrocarbons for the chemical synthesis industry.

Bituminous coal is a dense sedimentary rock, usually black, but sometimes dark brown, often with well-defined bands of bright and dull materials. It is used primarily as fuel in steam-electric power generation, with substantial quantities used for heat and power applications in manufacturing and to make coke.

Anthracite, the highest rank of coal, is a harder, glossy black coal used primarily for residential and commercial space heating. It may be divided further into metamorphically altered bituminous coal and "petrified oil", as from the deposits in Pennsylvania.

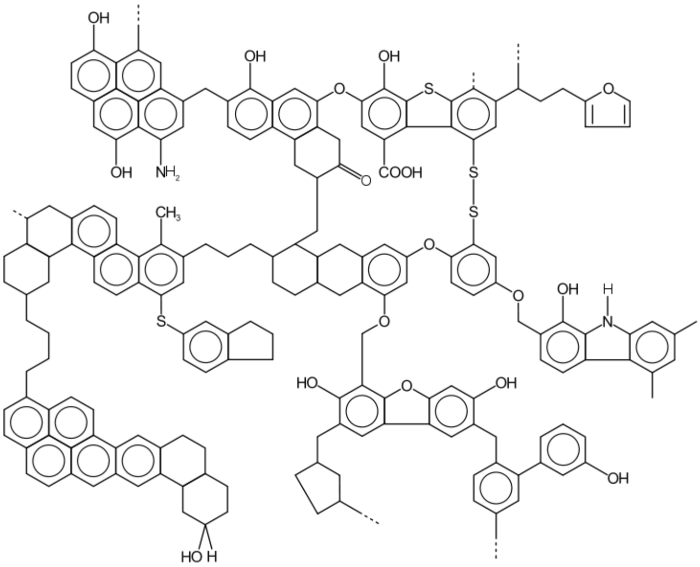


Figure 2.1 The example for chemical structure of coal [7]

2.1.2 Thermal decomposition of coal [8]

It is proposed that, in the thermal decomposition process as the coal particle temperature rises during thermal decomposition (which may also be the initial stages of the combustion process), the bonds between the aromatic clusters in the coal macromolecules break and create lower-molecular-weight fragments that are detached from the macromolecule the larger fragments of this decomposition process are often (collectively) referred to as the *metaplast*.

During pyrolysis, the metaplast will either vaporize and escape from the coal or be reincorporated into the residual macromolecule by chemical cross-linking. The portion of the metaplast that is vaporized usually consists of the lower-molecular-weight fragments and distills from the hot zone as *tar*. Side chains on the aromatic clusters are released from the coal as light gases. These light gases are generally carbon monoxide (CO), carbon dioxide (CO2), water (H2O), and low-molecular weight hydrocarbons (C1–C4 and up to C8 or C10).

The pyrolysis behavior of a coal is a strong function of coal type or rank. Low-rank coal (such as lignite and sub-bituminous coal) produces relatively high levels of low-molecular-weight gases and very little tar. Bituminous coal produces significantly more tar than low-rank coal and moderate amounts of light gases. High-rank coal produces relatively low levels of both light gases and tar.

Thus, coal undergoes a large variety of physical and chemical changes when heated to temperatures where thermal decomposition occurs. However, some changes may be noted before the onset of what is often referred to as thermal decomposition proper (i.e., carbon–carbon bond scission and the like) and may manifest themselves as the formation of low-molecular-weight species

For example, while the temperature of the onset of thermal decomposition proper is generally recognized to be approximately 350 °C (called cracking temperature), water will appear as a product of heating coal at temperatures below 100 °C. In addition, when a coal is “degassed” at temperatures below 100 °C, adsorbed methane and carbon dioxide will appear as “products” of the thermal treatment. On the other hand, a coal such as lignite, which contains many carboxylic functions as part of the coal structure, will evolve carbon dioxide by thermal decarboxylation:

$$RCO_2H \longrightarrow RH + CO2$$

Such changes are usually noted to occur at temperatures just in excess of 100 ^{o}C and more than 50% of the carboxylic acid functions can lose carbon dioxide over the temperature range 100 °C–200 °C. As the temperature of the thermal treatment is increased to the range 200 °C–370 °C, coals lose a variety of lower-molecular-weight organic species (especially aliphatic compounds), which are believed to arise from moieties that are “loosely bound” to the more thermally stable part of the coal structure. Some of the lower-molecular-weight aromatic species may also be obtained. At higher temperatures (i.e. 370 °C; 700 °C), methane (indicative of the thermal destruction of the coal structure), polycyclic aromatics, phenols, and nitrogen compounds are produced.

With respect to the volatile matter produced by the thermal decomposition of coal, rapid thermal decomposition enables the production of lower-molecular-weight hydrocarbons along with the char residue. For bituminous coals, the decomposition increases markedly above 400 °C and reaches a maximum in the range 700 °C–900 °C. The yield of volatile matter in this process is a function of the coal type and ranges from approximately 20% w/w of the coal for a low-volatile bituminous coal to somewhat more than 55% w/w of the coal for a high-volatile C bituminous coal. Sub-bituminous coals may not show a volatile matter peak with increasing temperature. In addition to tarry products, the rapid pyrolysis of coal produces gases, such as hydrogen, methane, and carbon monoxide, as well as lesser amounts of hydrocarbons. Pyrolysis of coal is generally defined as the thermal decomposition of coal in the absence of air or other added substances.

2.1.3 Pyrolysis of coal [8]

Pyrolysis is the thermochemical decomposition of coal (and organic material in general) at elevated temperatures in the absence of oxygen. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C. The pyrolysis process generally produces gas and liquid products and leaves a solid residue richer in carbon content.

Coal pyrolysis is a complex process involving a large number of chemical reactions and the process occurs with the production of gas, liquor (low-molecular weight liquids), tar (high-molecular weight liquids), and char (coke). There is some variation of the product distribution with the temperature of the decomposition (Figure 2.2).

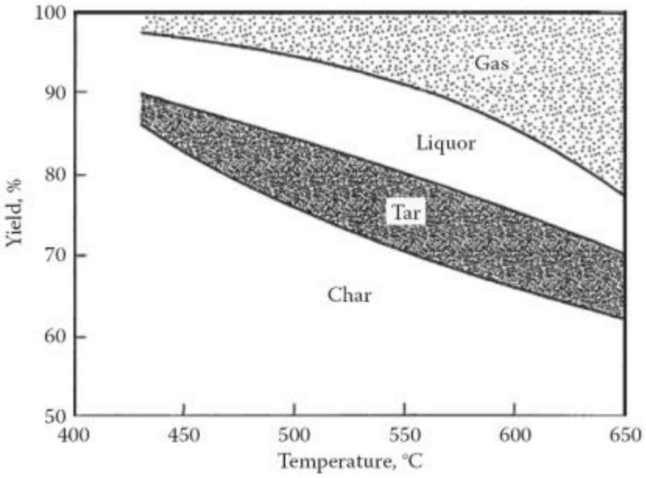


Figure 2.2 Distribution of products from coal carbonization at various temperatures [7]

The heterogeneous nature of coal and the complexity of the pyrolysis process have made it very difficult to perform unambiguous experiments to determine the rates and mechanisms in coal pyrolysis. In tar formation and transport, a consensus is being reached on the central role of the volatility of tar molecules in explaining the variation in operating conditions (pressure, heating rate, particle size, etc.) of the amounts and molecular weight distributions of tars. The role of heating rate on the onset of volatile evolution, volatile yield, product composition, and, to a lesser extent, coal type and particle size were found to be well established. As heating becomes more rapid, the onset of devolatilization shifts to much smaller timescales and to much higher surface temperatures. However, the role of heating rates on coal thermal properties was not found to be well understood.

In fact, each particular coal will have a definite decomposition temperature (although the general thermal decomposition temperature is 350 °C, which will be marked by the steady evolution of gaseous products (and an increase in the rate of weight loss) and which can be decreased by pretreatment with organic liquids (i.e., extraction of the lower-molecular-weight species from coal). Pretreatment of the coal by oxidation increases (as expected) the yields of carbon oxides and water but the coking properties are reduced; conversely, pretreatment with hydrogen improves the coking properties. Finally, the yield of volatile products is also dependent on the particle size of the coal.

The thermal decomposition of coal in the presence of water (or steam) exhibits significant differences over “dry” decomposition. For example, lignite and the lower-rank coals appear to undergo “coalification” by treatment at 315 °C–350 °C in the presence of water. The effect of water is enhanced if the decomposition is carried out in a “vacuum” and may even be analogous to the stimulus provided by steam in increasing the volatility of heavy crude oils and residua during vacuum distillation

The thermal behavior of coal may also be investigated by use of the differential thermal analysis method. In this technique, the differential change in temperature that occurs when a coal is heated at a given rate is noted to that for a reference material. The derivative is plotted against temperature to produce the thermogram. A positive slope indicates an exothermic reaction whereas a negative slope indicates an endothermic reaction. For example, peat illustrates exothermic behavior that reaches a maximum at ca. 370 ^{o}C but the maximum is somewhat less pronounced for the higher-rank coals and there is a shift to increasingly higher temperatures. On occasion, an endothermic reaction may be observed in the thermogram at 120 °C–150 °C, and is attributed to the evaporation of the water.

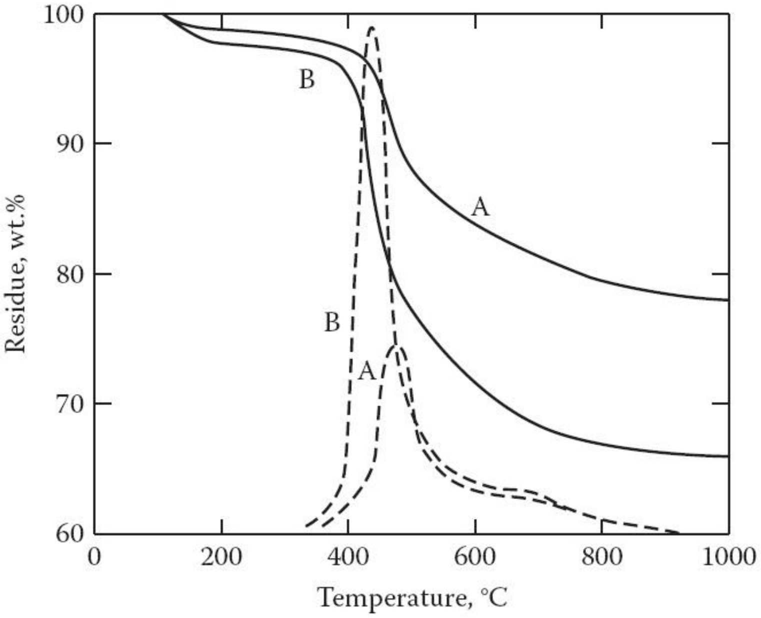


Figure 2.3 Thermogravimetric data for two coals (A and B) showing the respective integral curve and the derived curve [7]

In some coals, it has been observed that initial physical or chemical changes are associated with an endothermic reaction that may start at approximately 250 °C, and continue until approximately 410 ^{o}C–470 ^{o}C. While other the characteristic endothermic reactions may typically occur at temperatures between 410 ^{o}C and 610 ^{o}C, an endothermic reaction may be observed in the temperature range 750 ^{o}C–810 ^{o}C. On the other hand, thermal treatment of bituminous coal that contains a substantial amount of reactive macerals (such as vitrinite and exinite) shows an exothermic reaction accompanied by softening or plastic behavior followed by solidification. The mutagenicity of coal pyrolysis products depends on three factors: the chemical structure of the parent coal, pyrolysis temperature, and residence time, as a consequence of the differences in both specific mutagenicity of the pyrolysis products and their yields. Total mutagenicity exhibits the following order with coal type:

High-volatile bituminous > subbituminous > lignite >> anthracite

This order, which is similar to that of volatile matter in the parent coals, reflects the comparative yields of extractable material from the pyrolysis of these coals. Total mutagenicity peaks in a temperature range of 1025 °C–1225 °C for all four coals and generally parallels the temperature and residence time trends of aromatic yield. Mutagens form faster and are destroyed faster at higher temperatures. Specific mutagenicity varies with coal type and pyrolysis conditions, but differences exhibit only a secondary effect on total mutagenicity. Specific mutagenic activity reaches peak values at higher temperatures and longer residence times than organic yield. There is a competition between mutagen formation and mutagen destruction reactions that evinces itself in the residence time/temperature trends of total mutagenicity. Formation reactions prevail at low temperatures and short times. Destruction reactions prevail at high temperatures and long times. The resulting products reflect the relative dominance of one set over the other.

2.3 Biomass

Biomass is a general term for material or biological material derived from living organisms such as growing plants or animal manure. It is a quite simple term for all organic material that stems from plants, trees and crops. Biomass material has quite low volumetric density in comparison to that of coal. It typically contains more than 70% of air and void space. This low volumetric energy density makes it difficult to collect, transport, store and utilize. Biomass can be used directly (e.g. combustion) or indirectly by converted into convenient solid, liquid and gaseous fuels. There are many resources of biomass such as wood and wood wastes, agricultural crops and their waste by-product and/or herbaceous biomass. Biomass is a renewable and potentially sustainable resource which can be used for energy production and chemical or material production. [9], [10], [11]

2.3.1 Lignocellulosic biomass

Lignocellulosic biomass or Lignocellulose is a plant dry matter (biomass). It is raw material for the production of bio-fuels. It generalizes the structure of plants to the three main sugar-based polymeric structures, which are cellulose, hemicellulose (cellulose and hemicelluloses are the carbohydrate polymers) and lignin (aromatic polymers). These three polymeric structures are mainly considered in many studies for the understanding of decomposition mechanisms of woody and herbaceous biomass. [11]

2.2.2 Components of biomass

Generally, biomass contains absorbed and condensed moisture, some inorganic materials, and various types of organic compounds. The inorganic materials are present by ash content. Since the biomasses in this study are Lignocellulosic biomasses, so the main of organic compounds are cellulose, hemicellulose and lignin.

2.2.2.1 Moisture content [11]

Moisture is presented both as water is contained in the cavity within the dead cell and also as absorbed water. The water contained in the cavity within the dead cell can be removed by drying while the absorbed water equilibrates with the ambient relative humidity. The moisture content is normally expressed on a wet basis which refers to the weight of water as a percentage of the total wet fuel weight. The moisture content of biomass has a significant effect on its conversion efficiency and heating value. The heating of water and its conversion to steam requires heat which is generated from biomass combustion. This leads to longer heating time. Apart from loss of combustion efficiency, the high moisture content biomass has more of a tendency to decompose, resulting in energy loss during storage. Transportation of high moisture biomass is also costly, due to the larger space required and higher loaded weight.

2.2.2.2 Ash content

Ash content represents the inorganic materials that are non-combustible. The ash content can be expressed on a wet, dry, or dry ash-free basis. In general, the ash content is expressed on a dry basis. Ash is deposited within the biomass during plant growth which is varied according to the species, locality, and soil contamination. The composition of the ash affects its behavior under the high temperature application such as combustion, pyrolysis, and gasification. For example, molten ash may cause problems in combustion reactors.

2.2.2.3 Chemical compositions

In chemical terms, biomass is defined as a three dimensional biopolymer composite. It is composed of an interconnected network of cellulose, hemicelluloses, lignin, minor amounts of extractives and inorganic matter.

Cellulose is the main component of plant cell walls conferring structural support. It is the most abundant organic chemical in many biomass species. It is polysaccharide (carbohydrate polymer) having the generic formula $(C_6H_{10}O_5)_n$ and an average molecular weight range of 300,000 to 500,000. Cellulose is a glucan polymer of D-glucopyranose units, which are linked together by β-(1 → 4)-glucosidic bonds. The building block for cellulose is actually cellobiose, the repeating unit of a two-sugar unit as in Figures 2.4 and 2.5. Cellulose is insoluble in water, forms the skeletal structure of most terrestrial biomass, and constitutes approximately 50 % of the cell wall material.

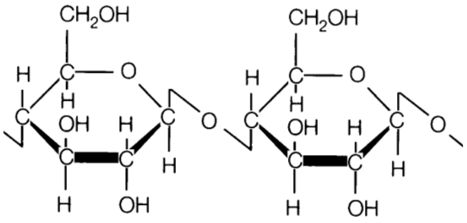


Figure 2.4 Chemical structure of cellobiose [11]

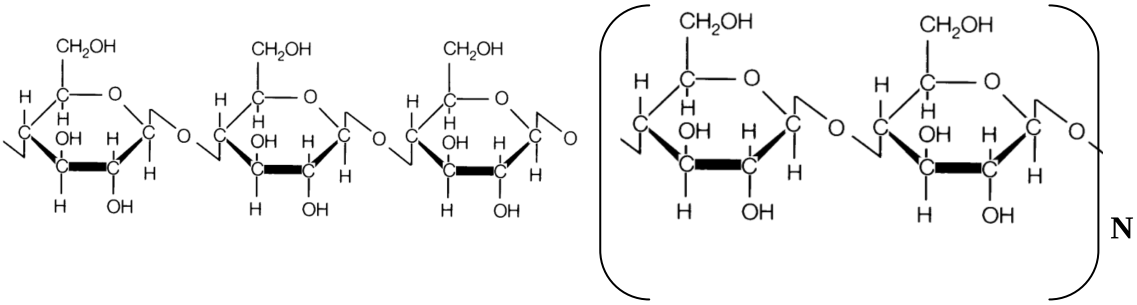


Figure 2.5 Partial structure of cellulose [11]

Hemicellulose is the second most abundant polymer (20–50% of Lignocellulose biomass) and differs from cellulose, because it is not chemically homogeneous. It is a group of polysaccharide polymers, which mainly are the sugars D-xylose, D-glucose, D-galactose, L-arabinose, and D-mannose, and D-glucuronic. The main hemicelluloses are shown in Figure 2.6. The structure of hemicelluloses can be understood by first considering the conformation of the monomer units. Hemicelluloses usually consist of 50 to 200 monomeric units and a few simple sugar residues. They are soluble in dilute alkali and consist of branched structures which vary significantly among different woody and herbaceous biomass species.

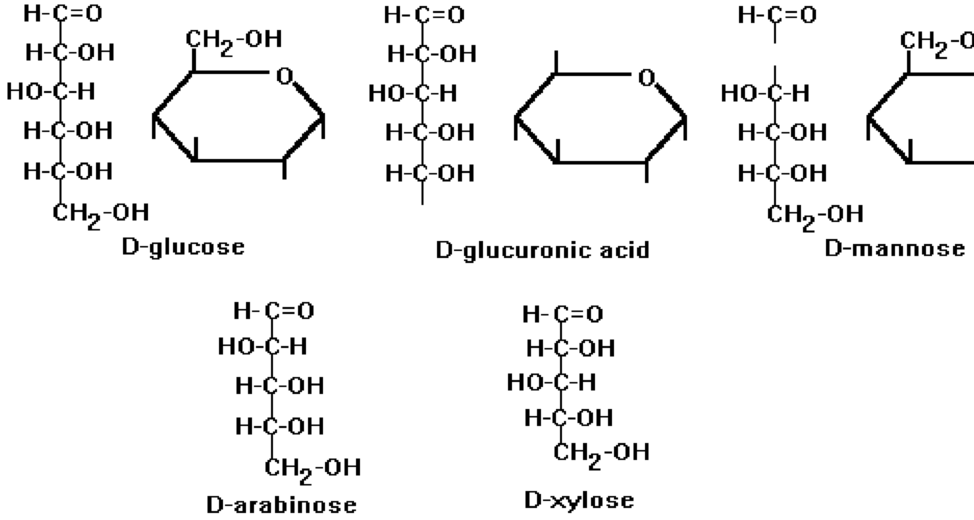


Figure 2.6 Sugar monomer components of wood hemicelluloses [11]

Lignin is the third most abundant polymer in nature. It is present in plant cell walls and confers a rigid, impermeable, resistance to microbial attack and oxidative stress. It is amorphous and highly complex. It mainly consists of aromatic polymers of phenylpropane units that are considered to be an encrusting substance. The linkages in the polymers occur directly between the rings, between the propane units, and through ether linkages via the hydroxyl groups. Lignin is generally found in the cell walls of certain biomasses, especially woody species. Apart from cell wall, it is often bound to adjacent cellulose fibers to form what has been called lignocellulosic complexes. Lignin can be classified in several ways, but they are usually divided according to their structural elements. All wood lignin consist mainly of three basic blocks of guaiacyl, syringyl, and *p*-hydroxyphenyl moieties. Lignin can be isolated from wood in several ways. So-called Klason lignin is obtained after hydrolyzing the polysaccharides with 72% sulfuric acid. It is highly condensed and does not truly represent the lignin in its native state in the wood.

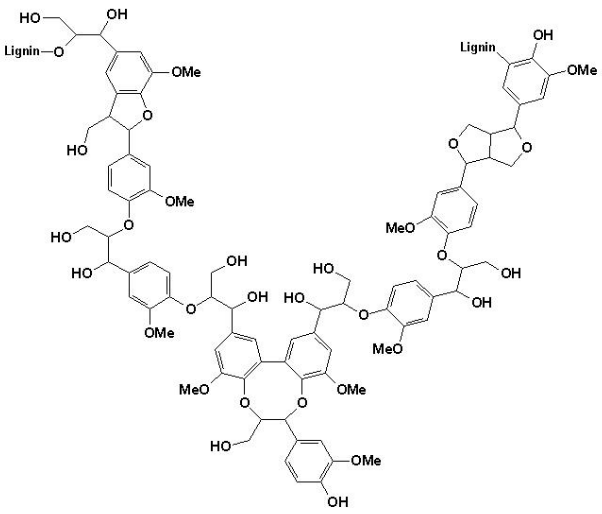


Figure 2.7 Small piece of lignin structure [11]

Extractives are chemicals in the wood that can be extracted by solvents. In some cases, the extractives are classified by the solvent used to extract them. The extractives are a group of cell wall chemicals, mainly consisting of fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes, and many other minor organic compounds. These chemicals exist as monomers, dimmers, and polymers. In general, softwoods have higher extractives content than hardwoods. Most of the extractives in both softwoods and hardwoods are located in the heartwood, and some are responsible for the color, smell, and durability of the wood.

2.1.3 Thermal decomposition of biomass

Thermal decomposition of the organic components is generally described by pyrolytic behavior. It heats the organic components in the absence of oxygen at mediate temperature. When biomass is heated to elevated temperature, it is pyrolysed and divided into a hydrogen-rich fraction and a carbon-rich solid residue (char). The hydrogen-rich fraction consists of gases and tar (volatile matter). Volatile matter is a mixture of low molecular weight compounds (hydrogen, oxides of carbon, methane, etc.) and higher molecular weight hydrocarbons, such as light oils and tars. The solid residue is a composite of the non-volatile or fixed carbon mixed with the inorganic mineral matter which will form ash upon oxidation. Pyrolysis is usually completed before significant gasification or combustion has occurred.

2.1.4 Pyrolysis of biomass [12]

In conventional pyrolysis or slow pyrolysis, cellulose and hemicelluloses are decomposed into volatile products and chars involving a series of highly complex reactions. These reactions may be classified in the following categories;

1) At temperatures below 300 °C, the pyrolysis of cellulose in an inert atmosphere proceeds through a series of reactions. The reactions include free radical initiation, elimination (of water), depolymerization, formation of carbonyl and carboxyl groups and evolution of CO and CO_2. The reactions in this temperature range produce mainly a char residue.

2) At the temperature range of 300-450 °C, the glycosidic linkages of the polysaccharide is broken by substitution involving one of the free hydroxyl groups to provide a mixture of levoglucosan, other derivatives of the glucose unit, and oligosaccharides.

3) At higher temperatures, dehydration, rearrangement, and fission of sugar units provide a variety of carbonyl compounds. The produced compounds, such as acetaldehyde, glyoxal and acrolein, readily evaporate. Condensation of the unsaturated products and cleavage of the side chains through a free radical mechanism leaves a highly reactive carbonaceous residue containing tapped free radicals.

Heating of the cellulosic material above 500 °C provides a mixture of all of these products. The addition of an acidic catalyst or slow heating promotes the dehydration and charring reactions.

2.2 Extraction of coal in a flowing solvent at temperature around 350 °C [2]

Miura explained the solvent extraction of coal. Recently solubilization or depolymerization experiments were conducted with various coals including eight Argonne premium coals at 200 °C to 400 °C using a flow-type reactor, where coal samples were heated in a flowing stream of solvent. The purpose of this work was to examine the coal structure through detailed analyses of the extract and the residue, and to examine the possibility of preparing clean fuels and/or raw materials for subsequent conversion.

The authors showed the image of the extraction method in Figure 2.8. Coal samples are heated up to around 350 °C from room temperature while a non-polar conventionally used solvent is continuously fed. At room temperature, coals are a little extracted. With increasing temperature, smaller molecule components start being extracted, and most of them are still soluble in the solvent when they are collected at the exit of room temperature. These components are called ‘‘soluble’’ hereinafter. With further increasing temperature, larger molecule components are gradually extracted, but those components are precipitated as solids when collected at room temperature. These components are called this fraction ‘‘deposit’’. Therefore, the products can be separated into four fractions by the proposed extraction method: soluble, deposit, residue, and gases.

Figure 2.9 compares the product yields obtained at the extraction temperature of 350 °C for eight Argonne premium coals. The yields of soluble and deposit for bituminous coals, Illinois #6 (IL), PITT (Pittsburgh #8), and UF (Upper Freeport) coals were very large. The extract yields for these coals are as follows: 80% (soluble: 41%, deposit: 39%) for UF, 67% (soluble: 29%, deposit: 38%) for PITT, and 63% (soluble: 27%, deposit: 36%) for IL. Surprisingly, 80% of UF coals were extracted at 350 °C. For the lowest rank coal, Beulah Zap lignite (ND), the deposit yield was very small and appreciable amounts of gaseous components were produced. Both the soluble and the deposit yields were small for the highest rank coal, Pochahontus (POC). These results indicate that decomposition reaction occurred for the lowest rank coal ND, but little decomposition reaction occurred for the other higher rank coals. Therefore, most of the soluble and the deposit for the higher rank coals are judged to be relatively low molecular weight components existent in the original coal. The small molecules could come out because the macromolecular network of coal was relaxed through the heat treatment in the solvent.

The most distinguishing result is that the soluble and the deposit contain little ash, which means that most of the ash remained in the residue. They have also estimated the molecular weight distribution (MWD) of the soluble, the deposit and the residue prepared from PITT coal. The MWDs for the raw coal, the residue and the deposit had peaks at M = ca. 300 and ca. 2200. On the other hand, the soluble consists of only small w molecules of less than 600 in M, and the peak position almost coincides with the peaks w of smaller M in the raw coal, the residue and the deposit. This presents the possibility w to prepare clean fuel or clean raw materials in a high yield from bituminous coals by simple extraction.

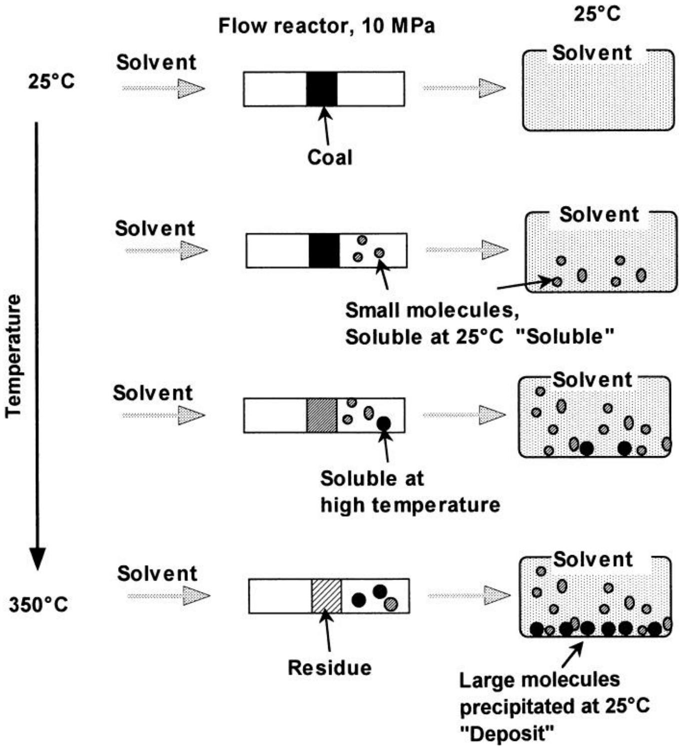


Figure 2.8 Image of the extraction of heated coal in a flowing solvent [2]

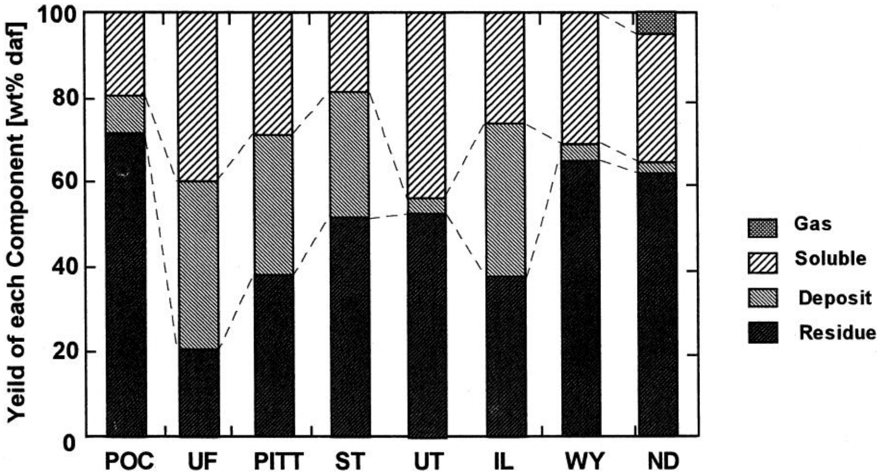


Figure 2.9 Product yields obtained at the extraction temperature of 350 °C for eight Argonne premium coals. [2]

2.7 Fundamentals of analytical instruments

2.7.1 Thermo-gravimetric Analyzer (TGA)

The analysis is performed involving the continuous measurement of a physical or chemical change in a sample. This technique is widely used for chemical analysis, and to simulate pyrolysis and combustion. In the experiment, a small quantity of powdered sample is heated on a highly sensitive microbalance in a given atmosphere. The experiment can be performed in an isothermal mode or in a non-isothermal mode. The change in weight of the sample is measured and plotted as a function of furnace temperature or time. The Thermo-gravimetric Analyzer apparatus used in this study was Perkin-Elmer, Pyris1 TGA.

2.7.2 Automatic Organic Elemental Analyzers (CHONS analyzers)

Analyses of organic compounds in which the common elements are carbon, hydrogen, oxygen, sulfur, and nitrogen are generally conducted in several experiments. The principle of analyses is based upon high-temperature decomposition of the organic compounds, which converts the sample to gaseous molecules. The gases are then separated by a chromatographic column or are based upon specific absorbents in some instruments. However, in most instruments, the thermal conductivity detection (TCD) is used as the detector for the final determinations. The Automatic Organic Elemental Analyzer used in this study was Thermo Finnigan, Flash EA1112 Series.

2.7.3 Gas Chromatography (GC)

Basically, chromatography involves adsorbing the sample onto some material called the stationary phase, while another phase, the mobile phase, is allowed to move across the stationary phase. Depending on the properties of the two phases and the components of the mixture, the mixture is separated into its components according to the rate at which each is removed from the stationary phase by the mobile phase.

In gas chromatography, the stationary phase consists of beads of an inert solid support coated with a high-boiling liquid, and the mobile phase is a gas, usually helium. The sample is injected by syringe onto a heated block where a stream of helium carries it onto a column packed with the stationary phase. The components of the mixture move through the column at different rates. Gas chromatography is also referred to as gas-liquid partition chromatography, because the technique depends on how different substances partition themselves between the gas phase (dispersed in the helium carrier gas) and the liquid phase (dissolved in the coating on the beads of solid support). After the components of a mixture are separated using gas chromatography, they must be detected at the exit of the GC column. The thermal-conductivity (TCD) and flame-ionization (FID) detectors are the two most common detectors on commercial gas chromatographs. Gas chromatography can also be used to identify the components of a mixture by comparing their retention times with those of authentic samples. This study used Shimadzu, GC-14B for pyrolysis gas products analysis.

2.7.4 Mass Spectrometry

Mass spectrometry is widely used because it provides the information about (i) the qualitative and quantitative composition of both inorganic and organic analysts in complex mixtures, (ii) the structures of wide variety of complex molecular species, (iii) isotopic ratios of atoms in samples, and (iv) the structure and composition of solid surfaces.

The concept that mass spectrometry examines is that an organic molecule is bombarded with high-energy electrons. From this bombardment, the energy is transferred as a result of dislodgement on the molecule's electrons.

$$\mathrm{A\!:B} \quad + \quad e^- \longrightarrow \mathrm{A}^{+}\cdot\mathrm{B} \quad + \quad 2e^-$$

Molecule Electron Cation radical Two electrons

In the above model, the molecule AB has been ionized by electron impact and the result is shown as the molecular ion, which is positively charged and has an odd number of electrons (cation radical). This molecular ion has the same mass as their original molecular form. At the same time, the excess used energy from the bombardment also further breaks the chemical bonds of molecular ions into smaller fragments. As a result, the cation radical is dissociation which produces a neutral fragment and a positively charged fragment.

$$\mathrm{A}^{+}\cdot\mathrm{B} \longrightarrow \mathrm{A}^{+} \quad + \quad \mathrm{B}\,\cdot$$

Cation radical Cation Radical

Considering the mass spectrometer, a very small amount of sample is introduced and converted to gaseous ions by the volatilization. Then the sample is bombarded with high-energy electrons resulting in the stream of positively charged ions, which are then accelerated into an analyzer tube surrounded by a magnet. This magnet deflects the ions from their original trajectory, causing them to adopt a circular path, the radius of which depends on their mass-to-charge ratio (*m/z*). Ions of small *m/z* are deflected more than those of larger *m/z*. By varying the magnetic field strength, ions of a particular *m/z* can be selectively focused through a narrow slit onto a detector. Scanning all *m/z* values at a detector gives the distribution of positive ions which is also called a mass spectrum and considered as the characteristic of a particular compound. The TG-MS used in this study was Perkin Elmer Clarus 500.

CHAPTER 3

METHODOLOGY

3.1 Selected solvent

1-Methylnaphthalene

The solvent was used as provided by SAFC 90 % purity. This Colorless liquid was used as the reference solvent, due to the wide availability of information in degradative solvent extraction. Its chemical structure is represented in Figure 3.1. 1-Methylnaphthalene is derived from coal tar. Boiling point and molecular weight of 1-MN is 240-243 °C and 142 g/mol, respectively. This solvent is well known as a non hydrogen donor solvent and non- polar solvent. This solvent does not react with the sample at about 350 °C, this property is very important for the degradative solvent extraction method.

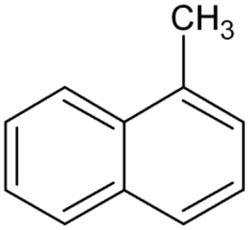


Figure 3.1 Chemical structure of 1-Methylnaphthalene

Biodiesel

Biodiesel or B-100 used is Palmitic Acid methyl ester, which is derived from palm oil. The chemical structure is showed in Figure 3.2. Boiling point and molecular weight of B-100 is 185 °C (at 10 mmHg) and 270.5 g/mol, respectively. The functional group of B-100 is alkyl group which its property quit be stability. It is so interesting to be used in this work.

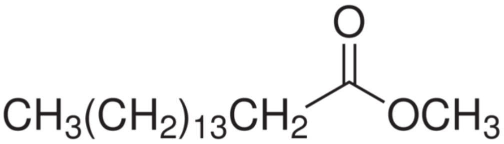


Figure 3.2 Chemical structure of B-100

WS2060

WS3060 is the solvent supplied by PTT Company.

3.2 Samples preparation

Coal (Sub-bituminous coal from PTT) and two biomasses (*Leucaena from Saraburi province and rice straw from Chiang Mai* province) were used in this study. The coal which is obtained from PTT is showed in Figure 3.3 and the size is about 0-5 mm. Coal samples were crushed into the size less than 500 µm. for degradative solvent extraction experiment. The prepared coal sample is shown in Figure 3.4.

Figure 3.3 Coal

Figure 3.4 Prepared coal

Raw leucaena and rice straw are shown in Figures 3.5 and 3.6. The biomass samples, Leucaena and rice straw are cut into the size less than 500 µm. for degradative solvent extraction experiment. The prepared Leucaena and rice straw are shown in Figures 3.7 and 3.8, respectively. The selected sizes of coal and biomasses samples were dried in a vacuum oven at 70 °C for 24 hours before the experiment.

Figure 3.5 Leucaena

Figure 3.6 Rice straw

Figure 3.7 Prepared Leucaena

Figure 3.8 Prepared rice straw

3.3 Sample characterization

3.3.1 Analysis of chemical properties of raw coal and biomasses

1) Ultimate analysis and calorific value calculation

The ultimate analysis gives the composition of coal and biomasses in percentage by weight (wt %) of carbon (C), hydrogen (H), oxygen (O), sulfur (S), and nitrogen (N). Dried and ground biomass was analyzed in the CHONS analyzer. For this technique, a sample was burned in an excess of oxygen, and various traps collect the combustion products. The Automatic Organic Elemental Analyzer used in this study was Thermo Finnigan, Flash EA1112 Series, which is shown in Figure 3.9.

Figure 3.9 A CHONS analyzer used in this study (Thermo Finnigan, Flash EA1112)

2) Proximate analysis and thermal decomposition

Proximate analysis gives moisture, volatile matter, fixed carbon and ash content of biomass. The apparatus used in proximate analysis is a Thermal Gravimetric Analyzer (TGA). The oven dried samples with particle sizes less than 75 µm about 5 mg were heated in nitrogen stream from room temperature to 900 °C in order to quantify moisture and volatile matter. At 900 °C, the condition was changed into oxygen or air atmosphere in order to quantify fixed carbon from loss weight in oxygen atmosphere and ash from the remaining solid. The study of thermal decomposition can be obtained by plotting weight decrease and sample temperature. The TGA apparatus used in this study is Perkin-Elmer, Pyris1 TGA.

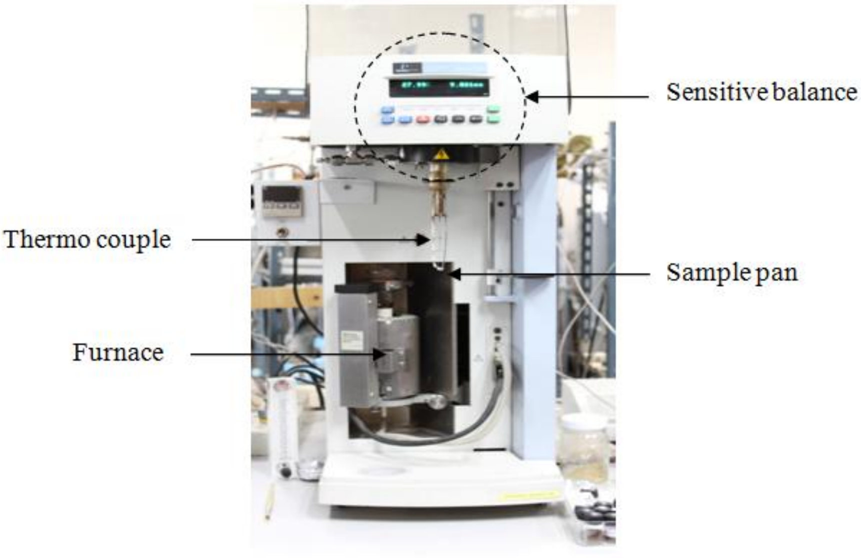


Figure 3.10 A TGA apparatus used in this study (Perkin-Elmer, Pyris1 TGA)

3.3.2 Chemical compositions or structural analysis

(1) Determination of extractives in biomass

Raw biomass is necessary to remove non-structural materials from biomass prior to analysis to prevent interference with later analytical steps. This consists of a two-step extraction process to remove water and ethanol solubles. Water soluble materials may include inorganic material, non-structural sugars, and nitrogenous material, among others. Ethanol soluble material includes chlorophyll, waxes, or other minor components. The results are reported, on a dry weight basis, as a weight percentage of the biomass.

The extractive in the biomass was determined by refluxing the ground biomass with ethanol reagent grade using the Soxhlet apparatus (AETM E1690). The raw biomass samples selected were between 75-150 µm and then dried at 70 °C over 24 hours. 2-10 g of sample was placed into an extraction thimble which was then placed on Soxhlet extraction apparatus. The reflux time necessary depends on the removal rate of components of interest, the temperature of the condensers, and the siphon rate. The solvent was removed when the reflux time was completed by using a rotary evaporator.

(2) Preparation of Holocellulose (Chlorite Holocellulose)

Holocellulose is the total polysaccharide (cellulose and hemicelluloses) content of wood, and the method for its determination is to remove all of the lignin from wood without disturbing the carbohydrates. The amount of holocellulose in biomass was examined by the Tappi Standard (T9). The amount of lignin in free extractive is removed by using acid chlorite solution.

(3) Preparation of alpha-cellulose (determination of hemicelluloses)

The dry holocellulose is treated with NaOH in order to remove hemicelluloses. The alpha-cellulose was obtained by using 17.5% NaOH (ASTM D 1103).

(4) Preparation of Klason lignin

The lignin contents of wood were examined by the Klason lignin method. The raw biomass sample was treated finely with 72% H_2SO_4. This procedure was followed by the Tappi Standard (T 222).

3.4 Study of Degradative solvent extraction in Parr reactor at temperatures below 350 ^{o}C

A tube reactor was used for the degradative solvent extraction in this study. Its size was 12 ml, 1.27 cm diameter and 15 cm inside depth. On each run, around 400 mg of sample on dry basis (d.b.) and 8 ml of solvent are charged in the reactor. Before the start of the heating, the reactor is purged by N_2 for several times, and then the reactor sealed with 1 psi of N_2 is heated to design temperature by sand bath. The sample is decomposed during the heat treatment, producing various products including gaseous product, water and low molecular weight compounds being dissolved in the solvent at the treatment temperature. After holding for 60 min and cooling to the room temperature, the gaseous product is collected in a gas bag then separates the liquid-like product from the solid residue by using stainless steel mesh (400 mesh). The liquid-like product was filtered with vacuum filter using PTFE 0.5 µm. in order to trapped the rest of residues that leave stainless steel mesh. The soluble in the filtrate is recovered as solid by removing the solvent using vacuum. The soluble and residue obtained is dried in a vacuum oven at 170-190 ºC until no solvent left, both of them is used for characterized purposed. The yields of all solid fractions and gaseous product were quantified from above.

Solid products (soluble and residue) were characterized by various analyses. The proximate analysis is made by using a thermogravimetric analyzer (Perkin-Elmer, Pyris1 TGA). The elemental analysis is performed on a CHN corder (Thermo Finnigan, Flash EA1112). The gas product analysis is performed on a gas chromatography (Shimadzu, GC-14B).

Figure 3.11 Tube reactor

3.5 Analysis

3.5.1 Product gas analysis

The collected gas product in the gas bag is immediately injected by 2 ml syringe into GC after the complete experimental condition was reached. The gas product was analyzed through TCD and FID detectors, respectively by using the porapak Q (PQ) column for methane and carbon dioxide analysis and the molecular sieve (MS-5A) column for carbon monoxide analysis. The GC apparatus used in this study was Shimadzu, GC-14B, which is shown in Figure 3.12.

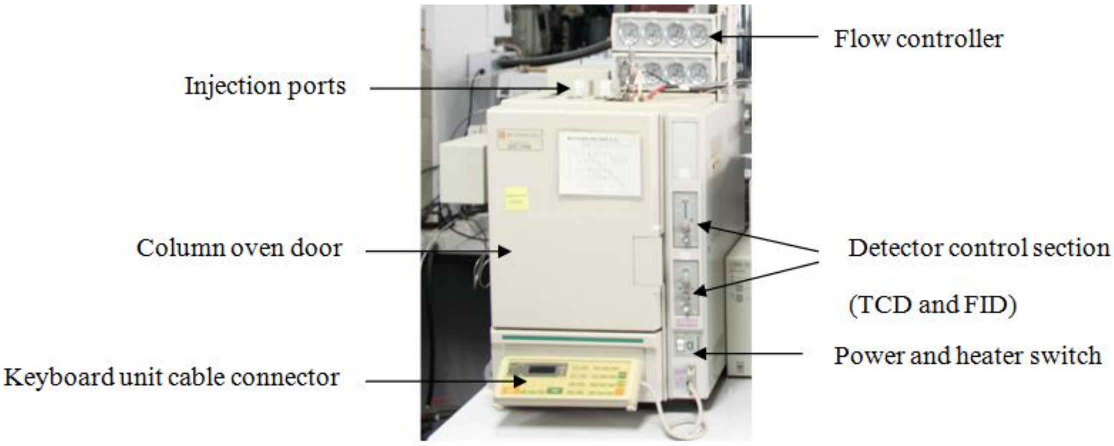


Figure 3.12 A GC apparatus used in this study (Shimadzu, GC-14B)

3.5.2 Characterization of the Soluble and Residue

- Ultimate analysis (CHN)
- Proximate analysis (TGA)
- Thermogravimetric (TG) curve (under nitrogen atmosphere at a heating rate of 10 ^{o}C/min
- Heating value (Bomb calorimeter)
- Functional group (FTIR)

CHAPTER 4

EXPERIMENTAL RESULTS

4.1 Raw samples analyses

4.1.1 Chemical properties analyses

The chemical properties of coal and biomass; elemental compositions, and proximate analyses were studied in this thesis work. The objectives of the chemical properties analyses were to understand the pyrolysis behavior and the thermal behavior in solvent treatment of each sample. Moreover, it can be used to identify the difference between raw samples and fractionation product (Soluble and Residue). The elemental compositions of raw coal and biomass were determined by ultimate analyses which give the composition of the samples in weight percentages of carbon, hydrogen, nitrogen and oxygen as well as sulfur (for coal). Table 4.1 presents the results of ultimate analyses including the proximate analyses of coal and biomass samples.

Table 4.1 Chemical properties analyses of coal and biomass samples

Raw sample	Ultimate analysis [wt%, d.a.f.]				Proximate analysis [wt%, d.b.]		
	C	H	N	O*	VM	FC	ash
Coal	63.3	5.0	1.0	30.9	52.9	40.4	6.7
Leucaena	47.7	6.2	0.7	45.4	82.6	16.0	1.4
Rice straw	47.0	6.5	0.6	45.9	67.5	15.9	16.6

The results show that carbon and oxygen were found as the major components for both coal and biomass. The element composition of this coal shows that the coal samples seem to be the low range coal. Raw coal has percentages of carbon content about 67.4 wt% on dry ash free basis which was higher than the percent of carbon in biomasses. Leucaena (LC) and Rice straw (RS) have percentages of carbon on dry ash free basis about 47.7 wt% and 47.0 wt%, respectively and have percentages of oxygen on dry ash free basis as high as

45.4 wt% and 45.9 wt%, respectively. Both biomasses look quite similar in term of elemental compositions but are different when compared by proximate analysis.

The proximate analyses of the samples were studied by thermal gravimetric analysis (TGA). In the experiment, about 5 mg of biomass sample was heated in nitrogen atmosphere from room temperature to 900 °C by 10 °C/minute heating rate. From TGA curve, the percentage of volatile matter was estimated from the weight loss at the temperature between 110 – 900 °C in nitrogen atmosphere while the percentage of fixed carbon was estimated from the weight loss at the 900 °C in air atmosphere and the percentage of ash was estimated from the weight remaining at 900 °C in air atmosphere. The proximate analyses results from TGA of raw coal and biomasses were presented in Table 4.1. Coal sample has quite high percentages of fixed carbon which were 41.2 wt% on dry basis. Volatile matter and ash contain in raw coal on dry basis were 53.4 wt% and 5.4 wt%, respectively. Fixed carbon of coal was higher than fixed carbon of biomass while volatile matter was the majority content of all biomass samples. Leucaena and rice straw have very high percentage of volatile matter which was 82.6 wt% and 67.5 wt%, respectively. For biomass samples, rice straw has high percentage of ash content which was 16.6 wt%, while Leucaena has very low percentage of ash content which was 1.4 wt%. This was as expected since Leucaena was a woody biomass which almost free from ash.

The pyrolysis behavior of coal and biomasses were studied by TGA curves to compare the weight decreasing of samples in gas phase pyrolysis and solvent treatment, and to understand the thermal behavior in degradative solvent extraction. Figure 4.1 compares the TGA curves of all studied samples. Pyrolysis behavior of coal and biomasses from TGA curve look much different, especially in dry ash free basis. From TGA curves, two biomasses (LC and RS) were decomposed at lower temperature compared with coal. Focusing at temperature around 350 °C, the weight decreases during gas phase pyrolysis were about 88.1 %, 30.7 % and 36.1 % for Coal, Rice straw and Leucaena, respectively. Due to the degradative solvent extraction involves the thermal decomposition, so the extraction yield from this method should be similar trend with pyrolysis behavior.

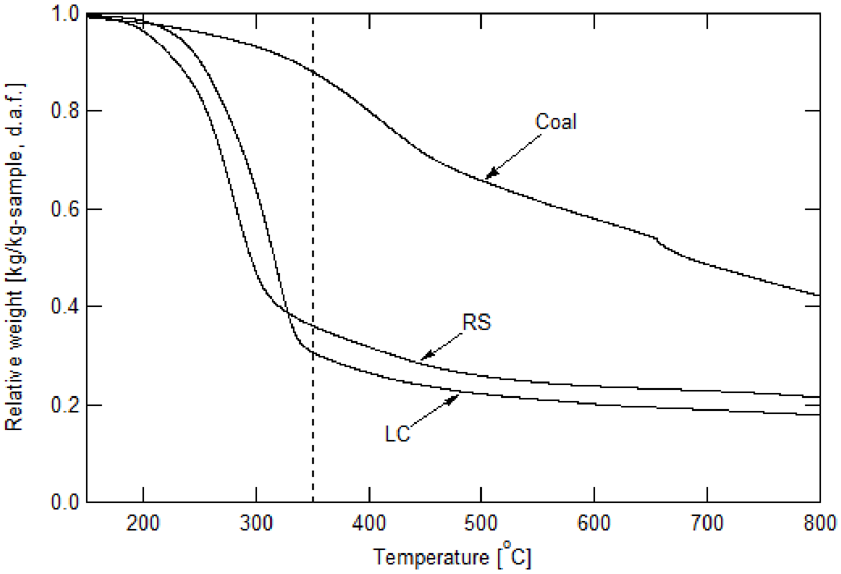


Figure 4.1 TGA curves of raw Rice straw, Leucaena and Coal

4.1.2 Chemical composition analyses

The chemical composition of biomass was highly variable because of its genetic and environmental influences. Although the elemental composition of Leucaena (LC) and Rice straw (RS) were quite similar, the chemical compositions of these two biomasses were significantly different. The chemical compositions of raw biomass samples were presented in Table 4.2. Leucaena (LC) has percentage of extractive about 10.1 wt%, while Rice straw (RS) has percentage of extractive which about 4.3 wt%. The percentages of cellulose of LC and RS were 39.9 and 35.1 wt%, respectively. Very different in hemicellolose, LC has high percentage of hemicellose (40.2 wt%), while Rice straw (RS) has percentage of hemicellulose which was only 22.5 wt%. The percentages of lignin of LC and RS were 27.5 and 20.3 wt%.

Table 4.2 Chemical composition analyses (wt%, d.a.f.) of biomass sample

Sample	Chemical composition analyses (wt%, d.a.f.)			
	Cellulose	Hemicellulose	Lignin	Extractive
Leucaena	39.9	22.5	27.5	10.1
Rice straw	35.1	40.2	20.3	4.3

4.2 Solvent Analyses

The treatment solvent plays a very important role in degradative solvent extraction. 1-Methylnapthalene was used as a model solvent. Two organic solvents, biodiesel from palm oil (B100) and WS3060 supplied from PTT Co., Ltd. were used as candidate solvents for the purposed in this research. WS3060 was the B100 and WS3060 were analyzed by GC-MS to identify the solvent compositions. Figures 4.2 - 4.3 show the intensity of B100 and WS3060 solvent. For B100 solvent, $C_{17}H_{24}O_2$ and $C_{19}H_{36}O_2$ were found as the major components of this solvent. $C_{12}H_{25}F$ found as the major components of WS3060 solvent. All three solvents were also analyzed by TGA (Figure 4.4) for comparing boiling of these solvents. During pyrolysis of WS3060, 1-MN and B100, each became totally gas phase at temperature about 130 °C, 170 °C and 239 °C, respectively. This result can be explained by the fact that the higher the molecular weight, the higher the phase-change temperature.

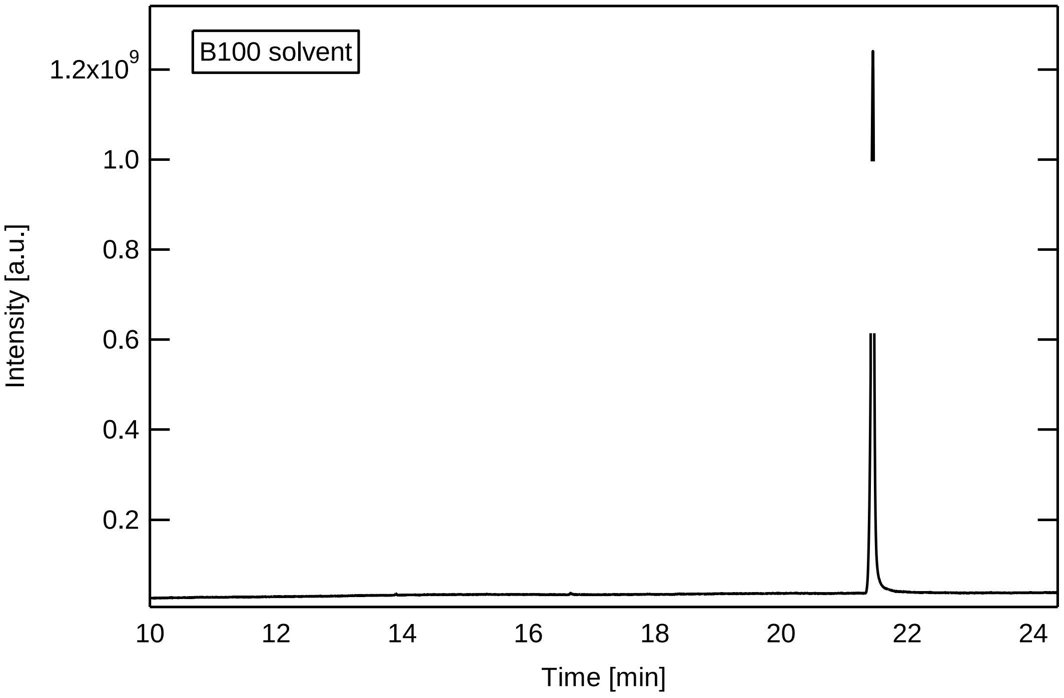


Figure 4.2 Intensity of B100 solvent

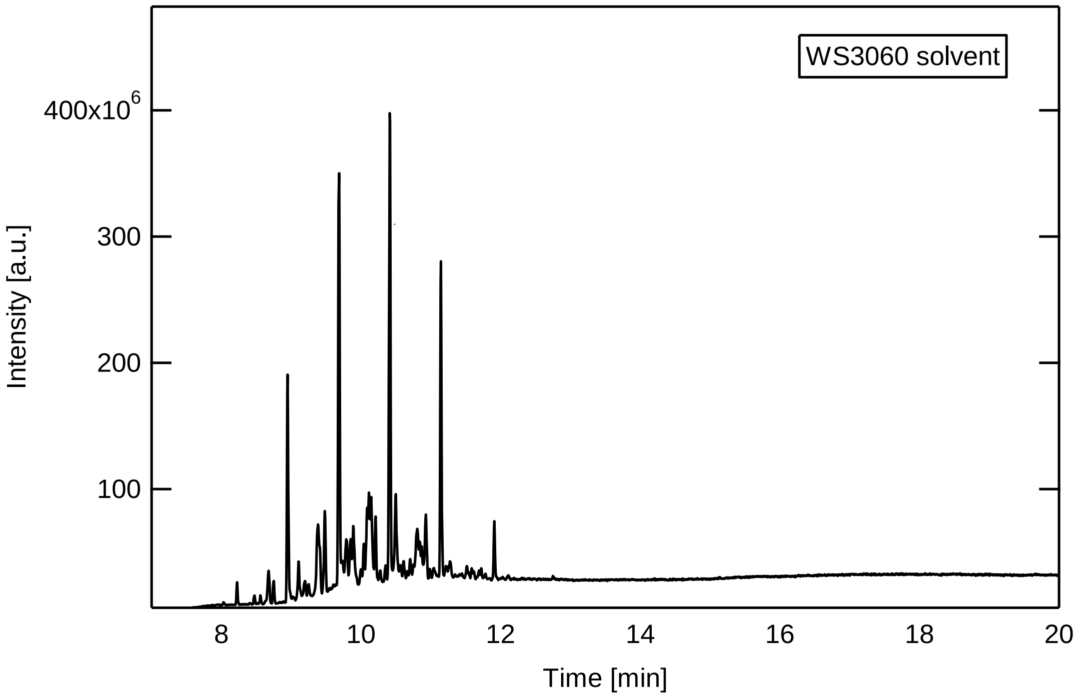


Figure 4.3 Intensity of WS3060 solvent

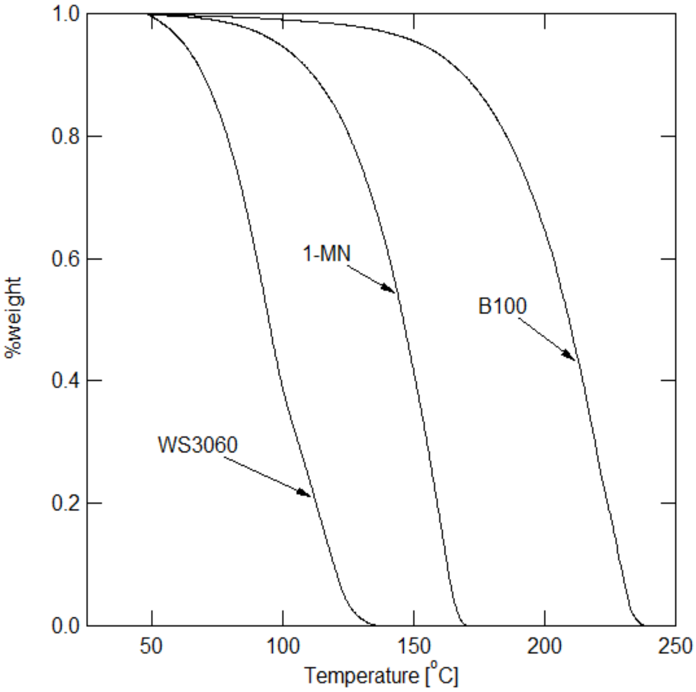


Figure 4.4 TGA curves of three solvents: 1-MN, B100 and WS3060

4.3 Degradative solvent extraction

4.3.1 Blank test experiment

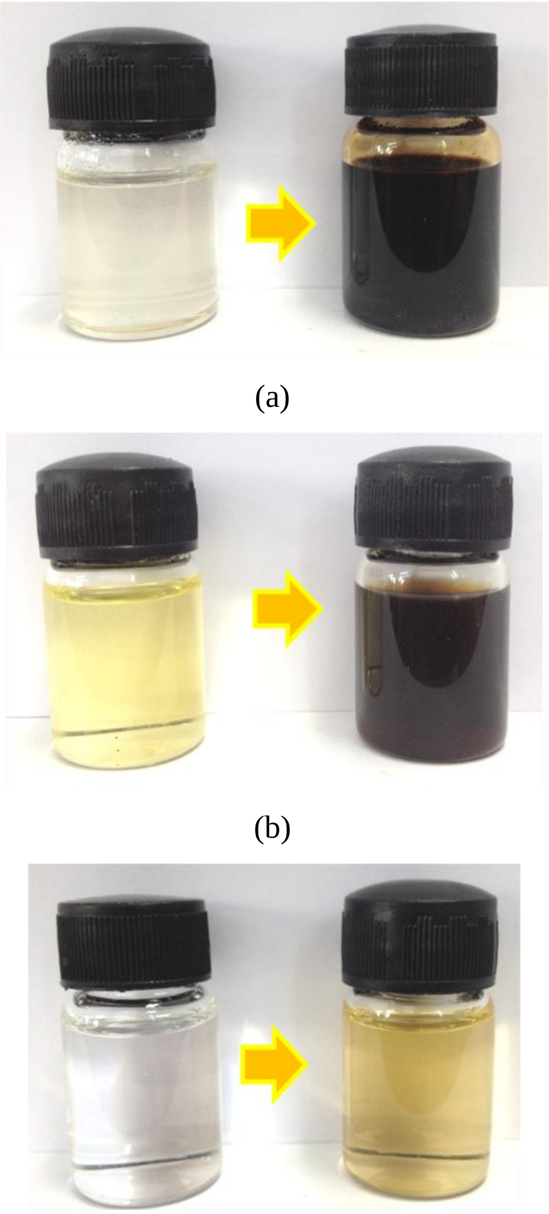
In the first step of degradative solvent extraction, 8 ml of three solvents, 1-MN, B100 and WS3060 were tested at 350 and 380 °C under pressure to checking for the generated gaseous from these solvents. The obtained data were used as the reference data for subtracting with the experiment with sample. The results showed that no gaseous product generated from 1-MN and WS3060 at all temperature. However, there was trace amount of gas produced from B100.

Table 4.3 Gaseous products from the solvents

Solvent (8 ml)	T (°C)	Yield (wt%)	Concentration of Gaseous product (Vol.%)				
			CO_2	CO	CH_4	C_2H_4	C_2H_6
1-MN	350	-			-		
	380	-			-		
B100	350	0.01	19.5	63.6	5.5	10.0	1.4
	380	0.05	20.0	64.6	5.8	5.5	4.0
WS3060	350	-			-		
	380	-			-		

4.3.2 Color of the solvent and extract

The color of the extract solution from rice straw by 1-MN, B100 and WS3060 at 350 °C are shown in Figures 4.5 (a), (b) and (c), respectively. The left was solvent before extraction. After upgrading rice straw by this method, the color of solvent changed. The color of extract from 1-MN solvent was black. The extract from B100 was lighter than 1-MN. For WS3060, the extract was not black. The color of extract can be shown the amount of carbon extracted.



(a)

(b)

(c)

Figure 4.5 The color of the extract from rice straw using (a) 1-MN, (b) B100 and (c) WS3060

4.3.3 Compare Extraction Yield from 1-MN, B100 and WS3060

First, the effect of the solvent on the product yield was examined at 350 °C using RS, LC and coal. 1-Methylnaphalene (1-MN), biodiesel from palm oil (B100) and WS3060 were used as solvent treatment. 1-MN was used for comparison purposes in this study. 1-MN is a non-polar and non hydrogen donor solvent. It is well-known and accepted in the field of direct coal liquefaction research that 1- MN is not involved in chemical reactions, even in the presence of a catalyst and hydrogen, at temperatures below 350 °C.

B100 and WS3060 were the organic solvents supplied by the PTT company for this study. The products yield obtain from these solvents were represented on weight basis for comparing. The yields of solid products were measured directly by weight and the yields and compositions of gaseous products were estimated from the gas chromatography. The extracted solution was recovered as a solid by removing the solvent and was called “Soluble”. The solid product retain after the reaction was call “Residue”. The yield of Liquid could not be directly measured, but the Liquid yield can be estimated from the mass balances. Figure 4.6 and 4.7 were shown the example of soluble and residue, respectively from RS after evaporation. Figure 4.8 (a), (b) and (c) showed the yields of extraction products on the dry and ash free (d.a.f.) weight basis from RS, LC and coal, respectively. Table 4.3 shows that the main gaseous products were CO2 and CO.

Figure 4.6 Soluble from rice straw using 1-MN

Figure 4.7 Residue from rice straw using 1-MN

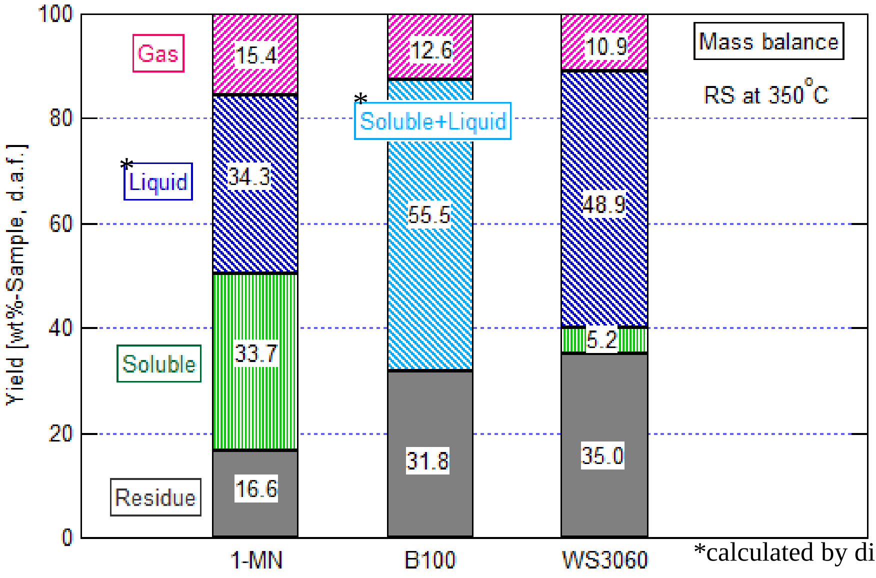
For RS, the yield of residues using 1-MN, B100 and WS3060 were about 16.6, 31.8 and 35.0 %, respectively. It was found that using 1-MN as a solvent obtains the lowest residue yield for RS. This result shows that 1-MN was very active for extraction. The gaseous products were about 15.4, 12.6 and 10.9 %, respectively for 1-MN, B100 and WS3060. The results show that these solvents can remove the oxygen functional group in the form of CO_2 and CO. In terms of the extracted product, the solubles from RS using 1-

MN and WS3060 were about 33.7 and 5.2 %, respectively. The soluble from WS3060 was very low when compared with 1-MN. The product from WS3060 was very large in “Liquid” product which calculated by different. The different in extraction product was probably from properties of solvent or interaction between solvent and sample. On the other hand, it was difficult to remove the solvent from the soluble fraction when B100 was used as a solvent. Therefore, the “Soluble + Liquid” fraction for B100 was quantified by the difference. The extraction yield from RS using B100, the Soluble + Liquid was about 55.5%.

The results for LC are shown in Figure 4.8 (b). The percentages of residues from LC using 1-MN, B100 and WS3060 were about 19.5, 31.6 and 34.8 %, respectively. The gaseous products were about 12.7 % for 1-MN, 12.2 % for B100 and 10.1 % for WS3060. The soluble from LC using 1-MN and WS3060 were about 34.2 and 6.2 %, respectively. For B100, the Soluble + Liquid was about 56.1%. The product yield occurred from LC quite be similar with RS for all of solvents.

Figure 4.8 (c) shows the product yield from coal. The percentages of residues from coal using 1-MN, B100 and WS3060 were about 19.5, 31.6 and 34.8 %, respectively. The residue yields from coal were significant higher than both biomasses. This result can be explained by the different properties between coal and biomass. From TGA curves of these samples, at 350 °C coal was degraded lower than both biomasses. The gaseous products were about 12.7 % for 1-MN, 12.2 % for B100 and 10.1 % for WS3060. The Liquid were about 12.7 % for 1-MN, 12.2 % for B100 and 10.1 % for WS3060. Gaseous and Liquid product from coal were lower than biomass because the oxygen in coal was very low. The soluble from coal using 1-MN and WS3060 were about 23.4 and 4.6 %, respectively. For B00, the Soluble + Liquid was about 16.0%.

Comparing the product yields from using the three solvents showed that the most effective solvent was 1-MN. The lowest residue yields were from using 1-MN as solvent for all of samples (both coal and biomasses). The samples can be degraded in 1-MN more than the degrading in gas phase condition. The extract which can be recovered to solid product (soluble) was very high yield when using 1-MN. Using WS3060 as solvent, the extraction yield was lower than 1-MN. Moreover the solid product recovered in term of soluble was very small amount. This probably because using WS3060 as solvents obtained smaller molecule product. Almost of the extract product became to Liquid fraction. The potential of using B100 as a solvent for degradative solvent extraction was examined. It was found that the gaseous products from B100, both from all of samples were not significantly different from using 1-MN. So the extract product will be studied in depth by element balance.



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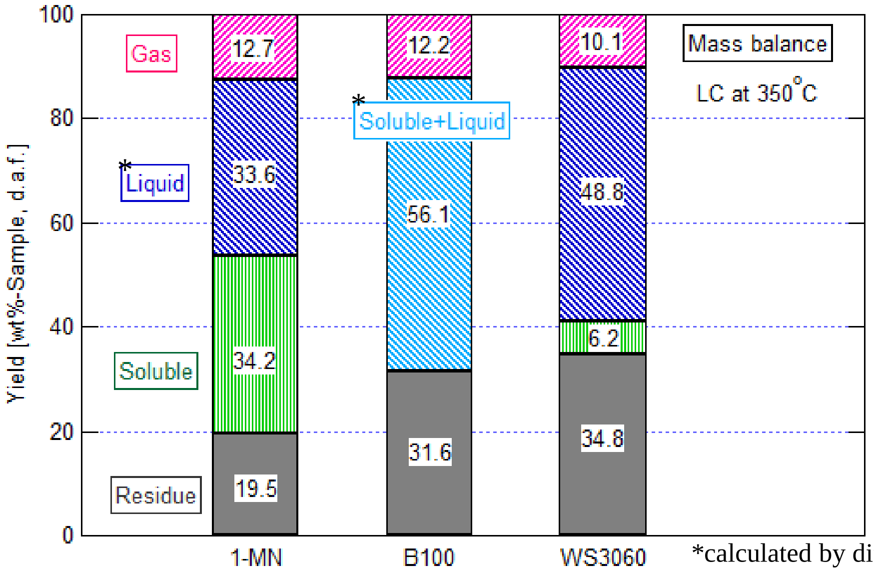
(a)



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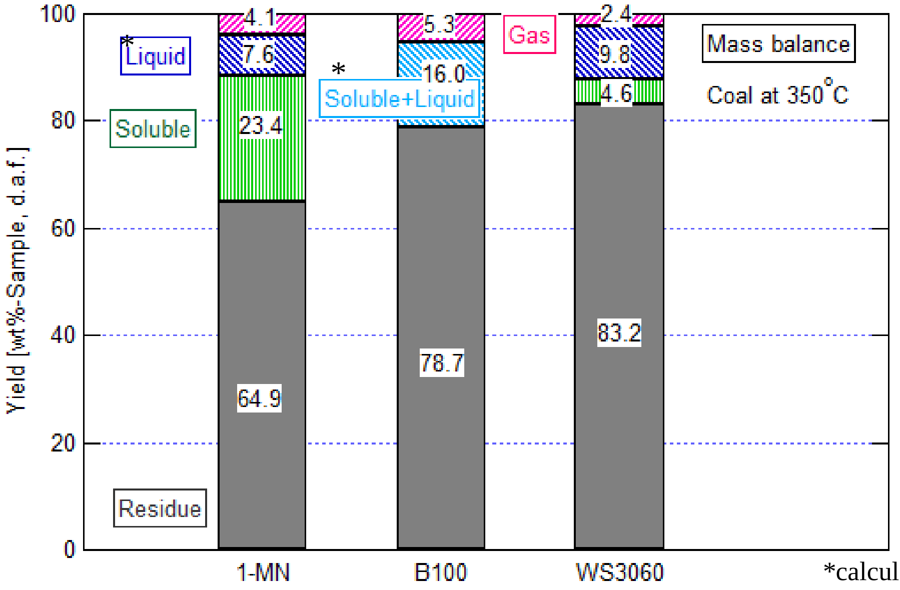

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Figure 4.8 Mass balances of product yields from (a) Rice straw, (b) Leucaena and (c) Coal by 1-MN, B100 and WS3060 solvent at 350 °C

Table 4.4 Gaseous products from Rice straw, Leucaena and Coal at 350 °C using three solvents

Gaseous product	Solvent	Yield [wt%]	Concentration of gaseous products (Vol.%)				
			CO_2	CO	CH_4	C_2H_4	C_2H_6
RS	1-MN	15.4	71.4	26.2	2.2	0.1	0.1
	B100	12.6	64.3	32.4	2.6	0.2	0.4
	WS3060	10.9	73.1	25.5	1.0	0.1	0.3
LC	1-MN	12.7	71.3	26.0	2.0	0.2	0.4
	B100	12.2	76.3	21.0	2.2	0.2	0.3
	WS3060	10.1	76.5	21.1	1.9	0.2	0.4
Coal	1-MN	4.1	89.2	8.2	2.4	0.1	0.1
	B100	5.3	83.9	9.4	5.9	0.5	0.3
	WS3060	2.4	88.6	8.1	2.9	0.1	0.3

4.3.4 Effect of solvent treatment temperature

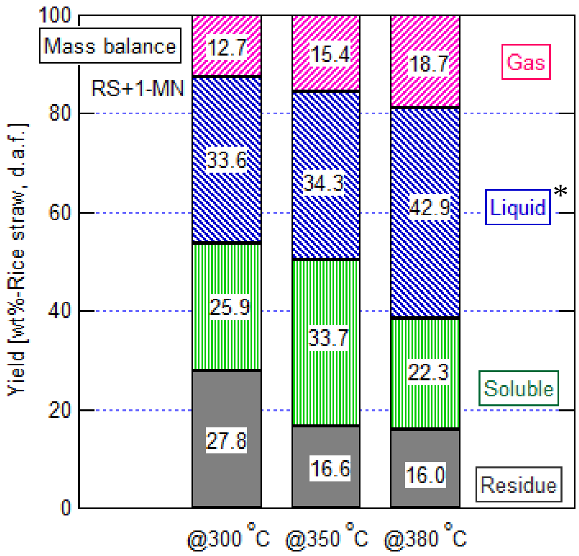
1) Product yield from 1-MN solvent

The product yield was studied at three temperatures using 1-MN solvent. Rice straw, Leucaena and Coal were examined. The results were shown in Figure 4.9. The product yields were reported on percentages yield on dry ash free basis and gaseous products were analyzed, as shown in Table 4.5.

RS was performed at 300, 350, and 380 °C at pressures of 16.1, 25.4 and 30.8 bars, respectively. From the results in Figure 4.9 (a), the product from rice straw (RS) using 1-MN solvent were shown in each fractions at three temperatures. The residue yields were about 27.8 %, 16.6 % and 16.0 % (wt%, d.a.f.) at 300, 350 and 380 °C, respectively. The soluble yields increased from 25.9 % to 33.7 % when increasing the temperature from 300 °C to 350 °C but when it was further increased to 380 °C the soluble yield decreased to 22.3 %. The gaseous products were about 12.7 %, 15.4 % and 18.7 % (wt%, d.a.f.) at 300 °C, 350 °C and 380 °C, respectively. The main gaseous products were carbon dioxide (CO_2) and Carbon monoxide (CO). The minor gaseous products were methane gas (CH_4) ethylene (C_2H_4) and ethane (C_2H_6). However, the weight percentage of methane in gaseous products significantly increased at 350 °C. It was showed that some of the extracted product might be degraded at this temperature. At 380 °C, although the residue product was decreased with increasing temperature, the soluble yield did not increase.

Similarly to RS, LC was performed at 300, 350, and 380 °C at pressures of 14.1, 20.7 and 30.6 bars, respectively. From the results in Figure 4.9 (b), the products from Leucaena (LC) using 1-MN solvent in each fraction were also shown at three temperatures. The soluble yields were about 29.0 %, 34.2 % and 31.7 % (wt%, d.a.f.) at 300 °C, 350 °C and 380 °C, respectively. The residue yields were about 28.1 %, 19.5 % and 14.6 % (wt%, d.a.f.) and the gaseous products were about 10.7 %, 12.7 % and 13.7 % (wt%, d.a.f.) at 300 °C, 350 °C and 380 °C, respectively. The main gaseous products were also CO_2 and CO. The change of product yield from LC with temperature was similar as that from RS. It can be concluded that when the temperature increased from 300 °C to 350 °C, soluble yields increased for both Rice straw and Leucaena, but when it was further increased to 380 °C, the soluble yield decreased. This was probably because the soluble were degraded to gaseous product and liquid product when the temperature was higher than 350 °C.

Coal sample was also performed at 300, 350, and 380 °C at pressures of 5.6, 8.4 and 11.6 bars, respectively. The pressures from coal were lower than biomass at all temperature due to coal had lower oxygen content. For coal sample, the products from Coal using 1-MN solvent were also shown in each fraction at three temperatures. The extraction yields from coal were different from biomasses. From the results in Figure 4.9 (c), the soluble yields were about 15.4 %, 23.4 % and 26.6 % (wt%, d.a.f.) at 300, 350 and 380 °C, respectively. When the temperature increased, the soluble yields of coal increased which was not similar to what happen with biomasses. The residue yields from coal were very high about 75.9 %, 64.9 % and 55.5 % (wt%, d.a.f.) at 300, 350 and 380 °C, respectively which decreased with increasing temperature. The gaseous products from coal were clearly smaller than gaseous product from biomasses, because the oxygen contents of coal were less than biomass samples.



(a)

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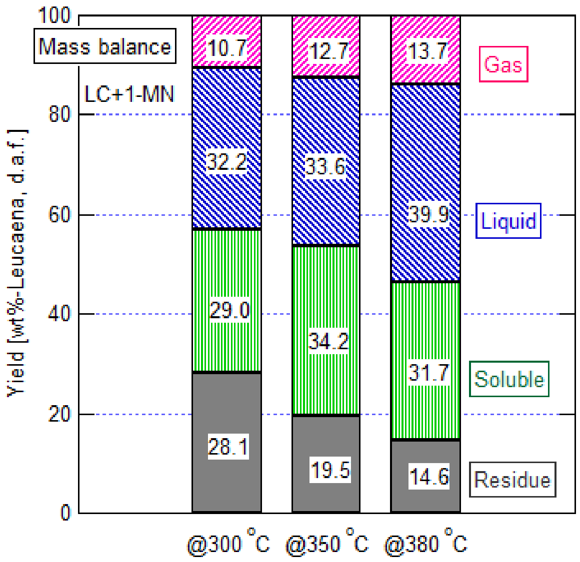

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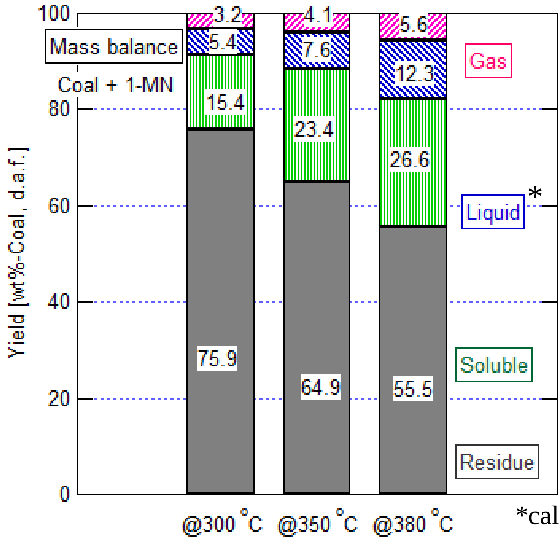

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(c)

Figure 4.9 Mass balances of product yields by 1-MN solvent with (a) Rice straw, (b) Leucaena and (c) Coal

Table 4.5 Gaseous products from Rice straw, Leucaena and Coal using 1-MN solvent

gaseous product (1-MN)	T (°C)	Yield (wt%)	Concentration of Gaseous product (Vol.%)				
			CO_2	CO	CH_4	C_2H_4	C_2H_6
RS	300	12.7	70.6	29.2	0.1	0.1	0.0
	350	15.4	71.4	26.2	2.2	0.1	0.1
	380	18.7	75.8	21.7	2.3	0.1	0.1
LC	300	10.7	79.4	20.3	0.1	0.1	0.1
	350	12.7	71.3	26.0	2.0	0.2	0.4
	380	13.7	66.3	28.8	4.2	0.1	0.6
Coal	300	3.2	94.3	2.9	0.7	0.1	0.0
	350	4.1	89.2	8.2	2.4	0.1	0.1
	380	5.6	83.9	10.7	4.9	0.1	0.4

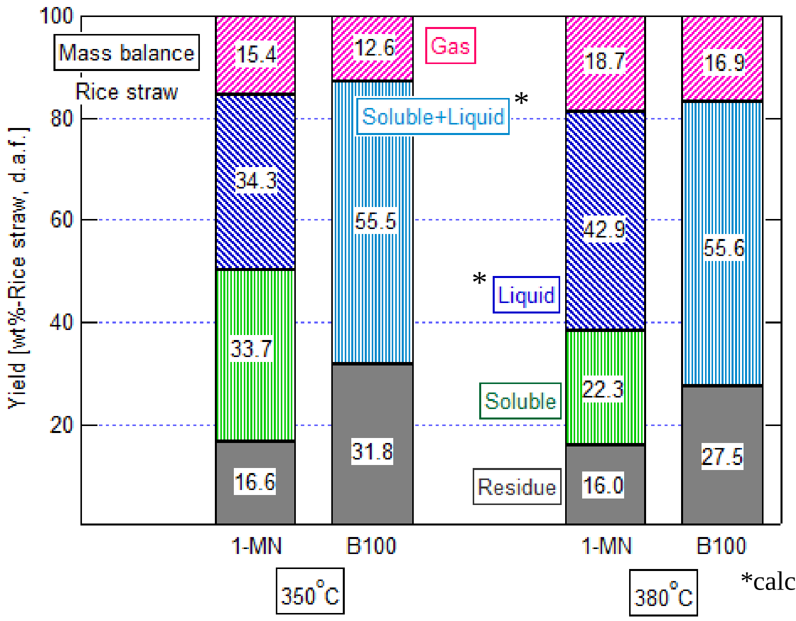
2) Product yield from B100 solvent

The study used biodiesel from palm oil or B100 was used as a solvent treatment for thesis. From the physical properties of this solvent had possibility that it did not react with the biomass sample at 350 °C. Biodiesel from palm oil (B100) was used as solvent treatment for the research purpose. Because the property of B100 was difference from 1-MN, it was difficult to remove the solvent from the soluble fraction when we used B100 as a solvent. Therefore, the extraction yield was reported by “Soluble + Liquid” fraction for B100 quantified by the difference. The product yield was studied at 350 and 380 °C using B100 solvent. Rice straw, Leucaena and Coal were examined. The results were shown in Figure 4.10. RS was performed at 350 and 380 °C with pressure 20.7 and 34.8 bar, respectively. From the results in Figure 4.10 (a), the product from rice straw (RS) using B100 solvent were separated into three fractions: gaseous product, Soluble+Luquid and Residue. The gaseous product were detected by GC analyzer and shown in Table 4.6. The residue yield which retained after the extraction was about 31.8% (wt%, d.a.f.) and decreased to 27.5% (wt%, d.a.f.) when increased temperature to 380 °C. The gaseous products also increased with temperature, it was found that the main gaseous products were CO_2 and CO which similar with 1-MN solvent. For the extraction yield, it was found that the “Soluble + Liquid” fraction was as large as 55.5 % and 55.6 % for 350 and 380 °C, respectively.

LC was performed at 350 and 380 °C at pressures of 20.0 and 34.1 bars, respectively. For Leucaena (LC), the product yields quite similar changed. From the results in Figure 4.10 (b), At 350 °C, th residue yield which retain after the extraction was about 31.6 % (wt%, d.a.f.) and decreased to 24.3% (wt%, d.a.f.) when increasing temperature to 380 °C. The main gaseous products were also CO_2 and CO which increased with increasing temperature. For the extraction yield, it was found that the “Soluble + Liquid” fraction were as large as 56.1 % and 61.0 % for 350 and 380 °C, respectively.

Coal sample was also performed at 350 and 380 °C at pressures of 6.9 and 22.4 bar, respectively. For the coal sample, extraction yields using B100 solvent were different from biomass. From the results in Figure 4.10 (c), at 350 °C, the residue yield which retained after the extraction was about 78.7 % (wt%, d.a.f.) and decreased to 69.4 % (wt%, d.a.f.) when increasing temperature to 380 °C. For the extraction product, Soluble + Liquid fraction were about 16.0 % and 22.4 % for 350 and 380 °C, respectively. The extraction yields from coal were smaller than the extraction yields from biomasses. The main gaseous products were also CO_2 and CO. It increased with temperature and lower than gaseous product from RS and LC at each temperature.

Comparing the extraction yields from B100 and 1-MN, B100 can be used as a solvent treatment since the weight percentages of the gaseous and residue products were quite similar. It was possible that B100 can extract the soluble product from the biomass but using the evaporator cannot remove B100 from soluble product. Therefore, to ensure that the product from B100 extraction was a soluble product, the residue product was further analyzed and studied by element distribution.



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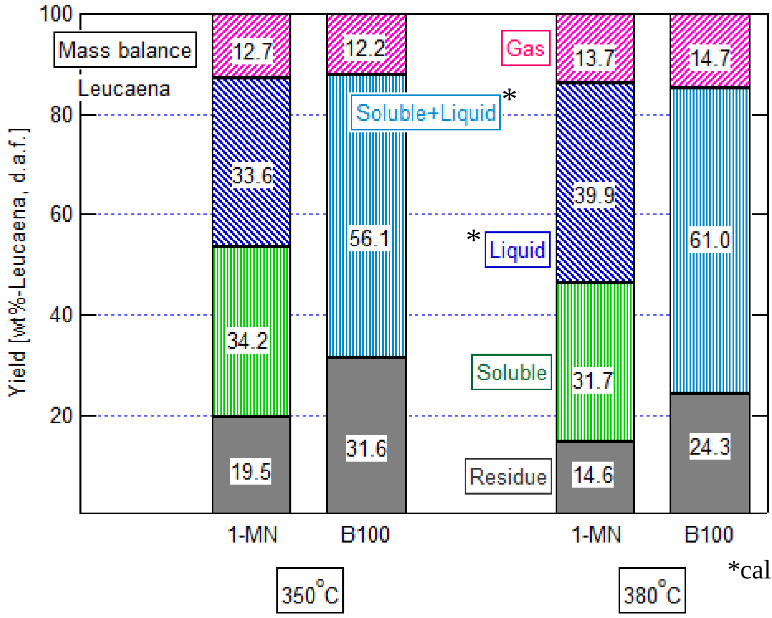
(a)



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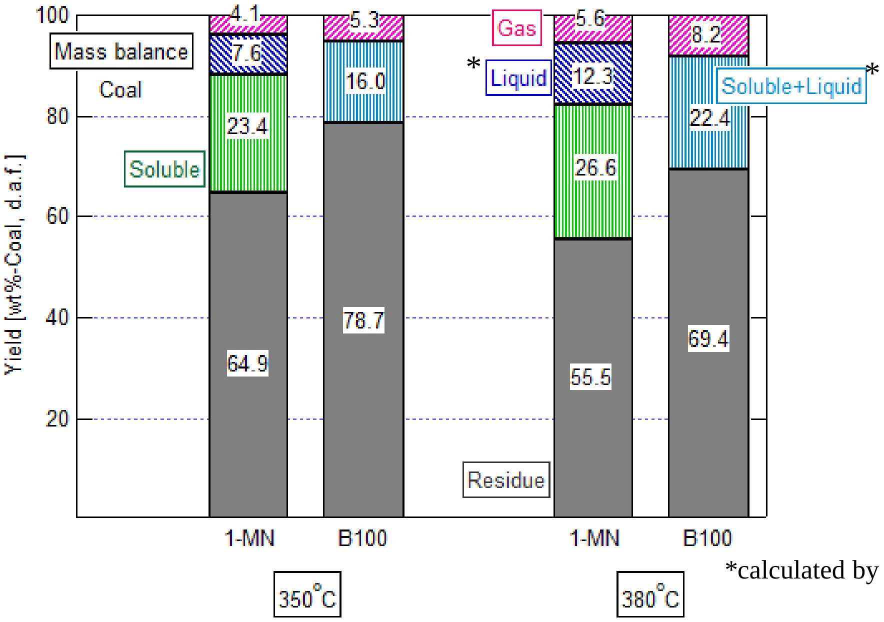

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(c)

Figure 4.10 Mass balance of products yields by B100 and 1-MN solvent with (a) Rice straw, (b) Leucaena and (c) Coal

Table 4.6 Gaseous products from Rice straw, Leucaena and Coal using B100 solvent

Gaseous product (1-MN)	T (°C)	Yield (wt%)	Concentration of gaseous products (Vol.%)				
			CO_2	CO	CH_4	C_2H_4	C_2H_6
RS	350	12.6	64.3	32.4	2.6	0.2	0.4
	380	16.9	68.7	24.3	6.0	0.1	0.9
LC	350	12.2	76.3	21.0	2.2	0.2	0.3
	380	14.7	69.1	23.4	6.7	0.1	0.7
Coal	350	5.3	84.0	9.4	5.9	0.4	0.3
	380	8.2	76.3	8.6	13.5	0.3	1.3

4.3.5 Element Distributions to products from 1-MN, B100 and WS3060

1) Element Distributions to product using 1-MN solvent

To examine the changes during the conversion of biomass, the elements distributed to each fraction were more informative than the weight basis yields. From the weight basis yields and elemental composition of products, all the product yields were calculated as the molar distributions of elements to the products on the basis of 1 kg of dried and ash free (d.a.f) samples as shown in Table 4.7. The tables gave the weight basis yields of products, the elemental compositions of the solid products, and the elements distributions of carbon, hydrogen, and oxygen to the products. In this study, all of product yields were also represented by weight percent distribution of elements to the products on dried ash free basis.

Table 4.4 gave the molar distributions of element to the product by using 1-MN solvent with RS, LC and coal at three temperatures of 300 350 and 380 °C. Figures 4.11 (a), (b) and (c), showed the element distribution by percentage weight for RS at 300, 350 and 350 °C, respectively.

Table 4.7 Product yields, ultimate analyses, element distributions to products obtained from RS, LC and Coal at three temperatures using 1-MN solvent

Sample	Yield [wt%, d.a.f.]	Utimate Analysis [wt%, d.a.f.]				Proximate Analysis [wt%, d.b.]			Elemental Balance [mol/g, d.a.f.]		
		C	H	N	O*	VM	FC	Ash	C	H	O
Rice straw	-	47.0	6.5	0.6	45.9	67.5	15.9	16.6	39.2	65.0	28.7
Treated at 300 °C											
Residue	27.8	65.1	4.8	1.1	29.0	38.8	21.6	39.6	15.1	13.4	5.0
Soluble	25.9	78.8	6.3	1.9	13.0	68.4	31.6	0.0	17.0	16.3	2.1
Gas	12.7	31.9	0.0	-	68.0				3.4	0.0	5.4
Liquid*	33.6								3.7	35.3	16.1
Treated at 350 °C											
Residue	16.6	68.1	5.4	0.9	25.6	37.6	19.2	43.2	9.4	8.9	2.7
Soluble	33.7	80.0	6.0	1.9	12.1	63.7	36.3	0.0	22.5	20.3	2.5
Gas	15.4	32.5	0.6	-	66.9			-	4.2	0.9	6.4
Liquid*	34.3							-	3.1	34.9	17.1
Treated at 380 °C											
Residue	16.0	68.8	5.4	1.0	24.8	35.7	19.0	45.3	9.2	8.7	2.5
Soluble	22.3	81.3	5.8	1.5	11.4	61.3	38.7	0.0	15.1	13.0	1.6
Gas	18.7	31.8	0.6	-	67.6				5.0	1.1	7.9
Liquid*	42.9								9.8	42.2	16.7

Table 4.7 Product yields, ultimate analyses, element distributions to products obtained from RS, LC and Coal at three temperatures using 1-MN solvent (Cont')

Sample	Yield [wt%, d.a.f.]	Utimate Analysis [wt%, d.a.f.]				Proximate Analysis [wt%, d.b.]			Elemental Balance [mol/g, d.a.f.]		
		C	H	N	O*	VM	FC	Ash	C	H	O
Leucaena	-	47.7	6.2	0.7	45.4	67.5	15.9	16.6	39.2	65.0	28.7
Treated at 300 °C											
Residue	28.1	70.2	5.3	1.6	25.8	66.0	28.4	5.6	16.4	15.0	4.0
Soluble	29.0	76.8	6.0	2.4	14.8	64.1	35.9	0.0	18.6	17.4	2.7
Gas	10.7	30.6	0.1	-	69.4				2.7	0.1	4.7
Liquid*	32.2								2.0	29.6	17.0
Treated at 350 °C											
Residue	19.5	73.1	5.4	1.5	20.0	55.2	38.1	6.7	11.9	10.6	2.4
Soluble	34.2	81.1	6.1	2.0	10.8	64.0	36.0	0.0	23.1	20.7	2.3
Gas	12.7	32.6	0.6	-	66.7			-	3.5	0.8	5.3
Liquid*	33.6							-	1.3	29.9	18.3
Treated at 380 °C											
Residue	14.6	74.0	4.6	0.9	20.5	42.8	48.9	8.3	9.0	6.7	1.9
Soluble	31.7	82.5	5.6	1.8	10.2	63.6	36.4	0.0	21.8	17.6	2.0
Gas	13.7	34.2	1.2	-	64.6				3.9	1.6	5.5
Liquid*	39.9								5.0	36.1	18.9

Table 4.7 Product yields, ultimate analyses, element distributions to products obtained from RS, LC and Coal at three temperatures using 1-MN solvent (Cont')

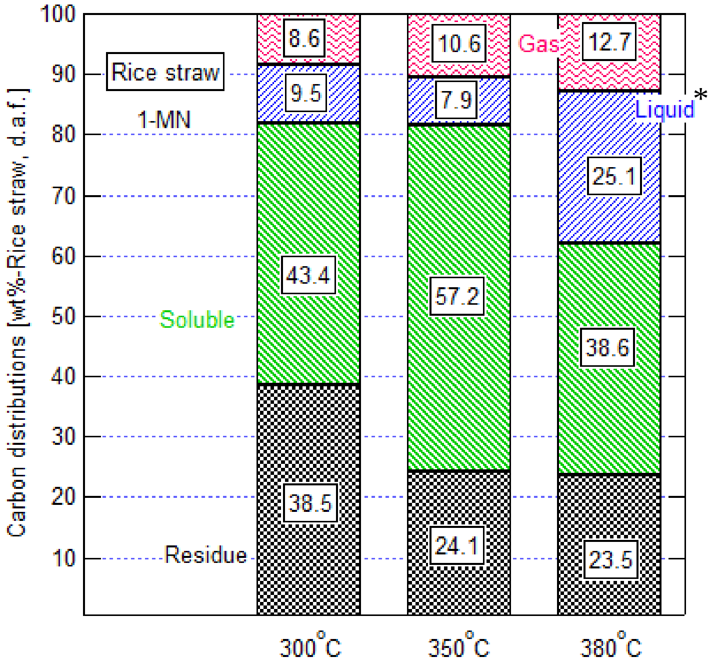
Sample	Yield [wt%, d.a.f.]	Utimate Analysis [wt%, d.a.f.]				Proximate Analysis [wt%, d.b.]			Elemental Balance [mol/g, d.a.f.]		
		C	H	N	O*	VM	FC	Ash	C	H	O
Coal	-	63.3	5.0	1.0	30.7	52.9	40.4	6.7	52.7	50.3	19.2
Treated at 300 °C											
Residue	75.9	66.1	4.1	1.5	28.3	50.5	42.3	7.2	41.8	31.2	13.4
Soluble	15.4	78.5	7.3	0.9	13.3	83.9	16.1	0.0	10.1	11.3	1.3
Gas	3.2	28.4	0.2	-	71.4				0.8	0.1	1.4
Liquid*	5.4								0.1	7.8	3.0
Treated at 350 °C											
Residue	64.9	66.7	3.8	1.6	27.9	47.2	44.6	8.2	36.1	24.8	11.3
Soluble	23.4	79.8	7.3	0.9	12.0	78.8	21.2	0.0	15.5	17.1	1.7
Gas	4.1	29.8	0.6	-	69.6				1.0	0.3	1.8
Liquid*	7.6								0.1	8.2	4.3
Treated at 380 °C											
Residue	55.5	70.4	3.8	1.5	24.3	41.8	48.3	9.9	32.6	21.0	8.4
Soluble	26.6	82.4	6.6	0.9	10.1	75.8	24.2	0.0	18.3	17.7	1.7
Gas	5.6	31.5	1.3	-	67.1				1.5	0.7	2.4
Liquid*	12.3								0.4	10.8	6.7

Table 4.7 clearly shows that the amount of oxygen in RS going to the gaseous product and Liquid increased with increasing treatment temperature. The amount of hydrogen going to Liquid and the amount of carbon going to the gaseous product also increased along with these changes. Since the main gaseous products were CO_2 and CO, the amount of hydrogen going to the gaseous product was very small. The molar ratio of hydrogen to oxygen going to Liquid was roughly 2 (shown in Table 4.4) at all of the treatment temperatures. From the results 75.1 %, 81.8 % and 85.8 % of oxygen was distributed to either gaseous product or Liquid at 300, 350 and 380 °C, respectively. These results showed that more than 80 % of oxygen was removed as CO_2, CO, and H_2O at temperature above 350 °C. At 350 °C, the carbon was distributed to Soluble and Residue, respectively by 57.4 % and 24.1 %, indicating that 81.5 % of carbon was retained in the solid product. The hydrogen was distributed to the gaseous product, Liquid, Soluble and Residue, respectively by 1.4 %, 53.7 %, 31.2 % and 13.7 %. Increasing the treatment temperature to 380 °C, the carbon was distributed to Soluble and Residue respectively by 38.6 % and 23.5 %. The carbon which retained in solid products was decreased. The hydrogen was distributed to the gaseous product, Liquid, Soluble and Residue, respectively by 1.7 %, 64.9 %, 20.1 % and 13.4 %. The carbon and hydrogen distributed to soluble were reduced in this temperature and lose to gaseous and liquid product.

The element distribution for LC is shown in Table 4.7. 76.4 %, 83.3 % and 86.3 % of oxygen was distributed to either gaseous product or Liquid at 300, 350 and 380 °C, respectively. More than 80 % of oxygen was also found to be removed as CO2, CO, and H2O at temperature above 350 °C. At 350 °C, the carbon was distributed to Soluble and Residue respectively by 58.2 % and 29.9 %, indicating that 88.1 % of carbon was retained in the solid product. The hydrogen was distributed to the gaseous product, Liquid, Soluble and Residue, respectively by 1.3 %, 48.2 %, 33.4 % and 17.1 %. Similar changed with RS, at 380 °C, the carbon distributed was decreased.

The element distributions through the products from coal are shown in Table 4.7 for 300, 350 and 380 °C, respectively. It was found that 23.2 %, 31.8 % and 47.3 % of oxygen was distributed to either gaseous product or Liquid at the above order temperature. These results showed that about 31.8 % and 47.3 % of oxygen were also found to be removed as CO_2, CO, and H_2O at 350 °C and 380 °C, respectively. At 350 °C, the carbon was distributed to Soluble and Residue respectively by 29.5 % and 68.5 %, indicating that 98.0 % of carbon was retained in the solid product. The hydrogen was distributed to the gaseous product, Liquid, Soluble and Residue respectively by 0.5 %, 16.2 %, 34.0 %, and 49.2 %. Increasing the treatment temperature to 380 °C, not similar with biomasses, the carbon was distributed to Soluble and Residue respectively by 34.6 % and 61.8 %. The carbon distributed to the soluble product was increased, and the carbon retained in the solid product was decreased only by 1.5%. Again at 380 °C, the hydrogen was distributed to the gaseous product, Liquid, Soluble and Residue respectively by 1.5 %, 21.5 %, 35.1 % and 41.8 %. These results show that more than 47.3 % of oxygen was removed as CO_2, CO, and H_2O at 380 °C while the carbon loss was very small.

It can be concluded that the 1-MN solvent was a very effective solvent for upgrading and fractionate both coal and biomass. The anticipated thermal reactions during the solvent treatment were deoxygenation reactions consisting of dehydration and decarboxylation. The results clearly show that more than 80 % of oxygen was removed from biomass at 350 °C and removed from coal at 380 °C by deoxygenation reactions. The loss of carbon to gaseous product was mainly due to the formation of CO2. For biomass, RS and LC, the largest yields among the solid products were soluble about 33.7 % and 34.2 % and their carbon based yields reached as large as 57.4 % and 58.2 %, respectively. These results clearly show that the proposed solvent treatment at above 350 °C was very effective to deoxygenate and simultaneously recover solid product having high carbon content and low oxygen content in rather high yield from biomass. For coal samples, at 380 °C, the soluble yield and it carbon based yields reached to 29.5 % and 34.6%, respectively. So, this temperature was effective when using 1-MN to extract coal.



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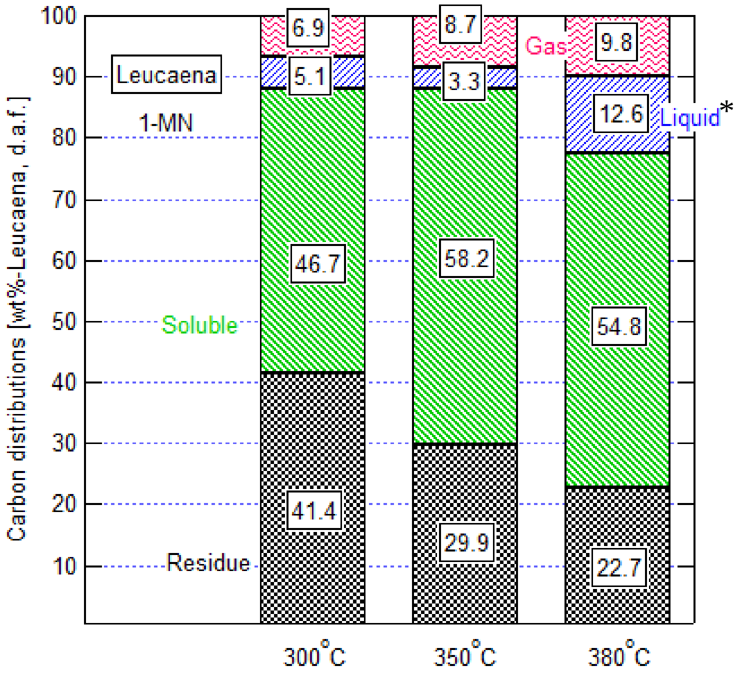
(a)



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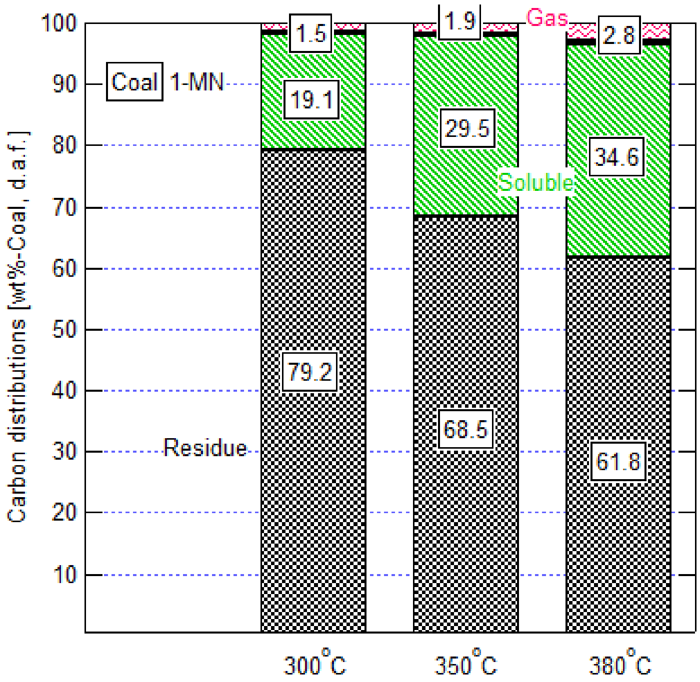
(b)



(c)

Figure 4.11 Carbon distributions to products using 1-MN from (a) RS, (b) LC and (c) Coal at 300 °C, 350 °C and 380 °C

2) Element Distributions to product from B100 solvent

The molar distributions of elements to the product by using B100 solvent with RS, LC and coal at 350 °C and 380 °C, are given in Table 4.6. Figures 4.12 (a) and (b) were shown the element distribution by percentages weight for RS at 350 °C and 380 °C, respectively. Because, it was difficult to remove the solvent from the soluble fraction when we used B100 as a solvent, so study in elemental distribution to products were more informative. Figure 4.15 clearly shows that the amount of oxygen in RS going to the gaseous product increased with increasing treatment temperature. At 350 °C, the carbon was distributed to Soluble+Liquid and Residue respectively by 43.5 %, and 47.4 %. When increased the treatment temperature to 380 °C, the carbon-based yields of the Soluble+Liquid fraction was increased to 45.3 %.

The element distributions for LC are shown in the Figure 4.12. At 350 °C, the carbon was distributed to Soluble+Liquid and Residue respectively by 46.1 % and 45.7 %. When increased the treatment temperature to 380 °C, the carbon-based yields of the Soluble+Liquid fraction was increased to 51.7 %.

The element distributions through the products from coal are shown in Figures 4.12 (b) and (c) for 350 and 380 °C, respectively. At 350 °C, the carbon was distributed to Soluble+Liquid and Residue respectively by 17.0 %, and 80.3 %. When increased the treatment temperature to 380 °C, the carbon-based yields of the Soluble+Liquid fraction was increased to 17.7 %.

From the results show that almost of gaseous products from using B100 were CO_2 and CO. This indicates that deoxygenation reactions by decarboxylation occurred during the treatment, similar with using 1-MN solvent. At 350, the carbon-based yields of the Soluble+Liquid fraction were 43.5 %, 46.1 % and 17.0 % for RS and LC and Coal, respectively, and increased to 45.3 %, 51.7 % and 17.7 % at 380 °C. These results show that the carbon can be extracted from the coal and biomass by using B100 solvent.

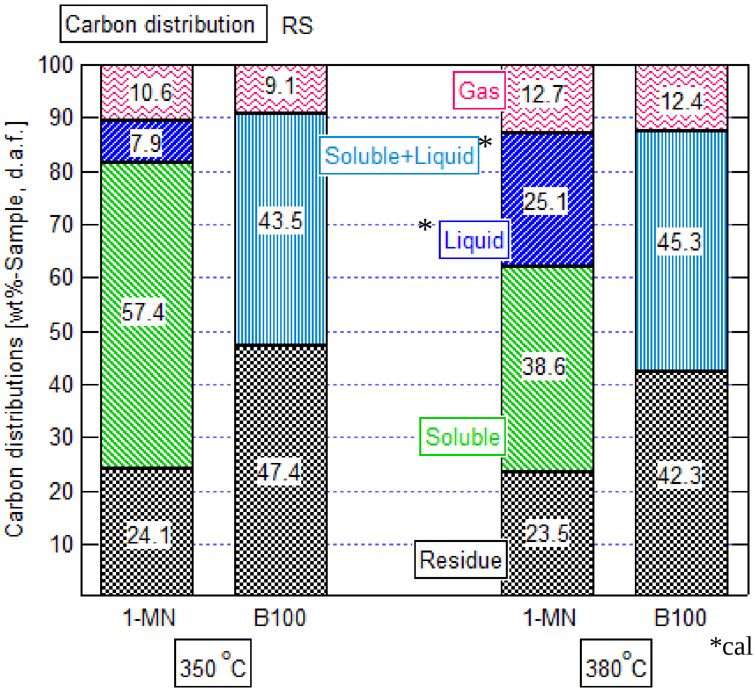
Table 4.8 Product yields, ultimate analyses, element distributions to products obtained from RS, LC and Coal at three temperatures using B100 solvent

Sample	Yield [wt%, d.a.f.]	Utimate Analysis [wt%, d.a.f.]				Proximate Analysis [wt%, d.b.]			Elemental Balance [mol/g, d.a.f.]		
		C	H	N	O*	VM	FC	Ash	C	H	O
Rice straw	-	47.0	6.5	0.6	45.9	67.5	15.9	16.6	39.2	65.0	28.7
Treated at 350 °C											
Residue	31.8	69.9	4.8	0.5	24.8	49.1	19.3	31.6	14.0	12.3	5.9
Gas	12.6	34.0	0.8	-	65.2				16.1	16.3	2.8
Soluble+Liquid*	55.5								3.4	0.0	5.4
Treated at 380 °C											
Residue	27.5	72.3	6.1	0.6	21.0	39.9	26.7	33.4	9.4	8.9	2.7
Gas	16.9	34.5	1.7	-	63.8				22.4	20.3	2.6
Soluble+Liquid*	55.6								4.2	0.9	6.4
Leucaena	-	47.7	6.2	0.7	45.4	82.6	16.0	1.4	39.8	62.0	28.4
Treated at 350 °C											
Residue	31.6	68.9	3.9	0.9	26.3	59.7	37.4	2.9	18.2	12.2	5.2
Gas	12.2	31.9	0.6	-	67.5				3.3	0.8	5.2
Soluble+Liquid*	56.1								18.3	49.0	18.0

Table 4.8 Product yields, ultimate analyses, element distributions to products obtained from RS, LC and Coal at three temperatures using B100 solvent (Cont’)

Sample	Yield [wt%, d.a.f.]	Utimate Analysis [wt%, d.a.f.]				Proximate Analysis [wt%, d.b.]			Elemental Balance [mol/g, d.a.f.]		
		C	H	N	O*	VM	FC	Ash	C	H	O
Treated at 380 °C											
Residue	24.3	74.0	5.0	0.8	20.2	54.5	41.1	4.4	15.0	12.2	3.1
Gas	14.7	34.5	1.8	-	63.7				4.2	2.7	5.9
Soluble+Liquid*	61.0								20.6	47.2	19.5
Coal	-	63.3	5.0	1.0	30.7	52.9	40.4	6.7	52.7	50.3	19.2
Treated at 350 °C											
Residue	78.7	64.6	3.0	1.2	31.3	50.2	42.4	7.4	42.4	23.5	15.4
Gas	5.3	32.0	1.6	-	66.4				1.4	0.9	2.2
Liquid*	16.0								9.0	25.9	1.6
Treated at 380 °C											
Residue	69.4	70.8	3.4	1.0	24.7	45.8	46.2	8.0	40.9	23.9	10.7
Gas	8.2	36.0	3.7	-	60.3				2.5	3.0	3.1
Liquid*	22.4								9.3	23.4	5.3

The carbon-based yields of RS, LC and coal from 1-MN and B100 were compared at 350 and 380 °C. At 350, the carbon-based gaseous yields from RS using 1-MN and B100 were very similar. Using B100 solvent, carbon retained in residue fraction was higher than using 1-MN. It can be concluded that the carbon extracted by B100 was lower than 1-MN.



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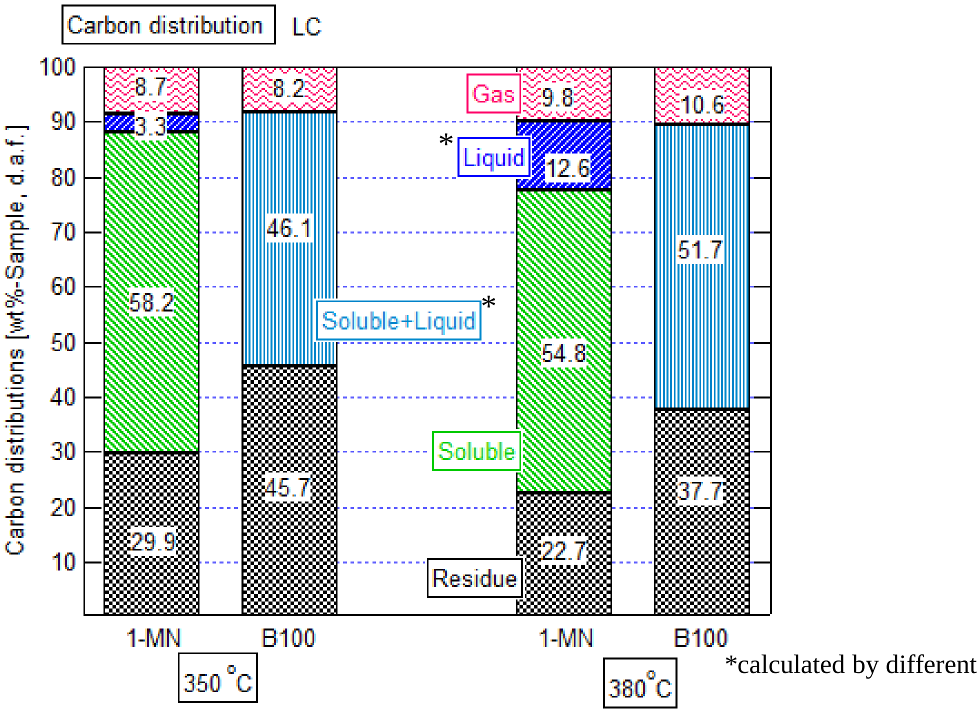
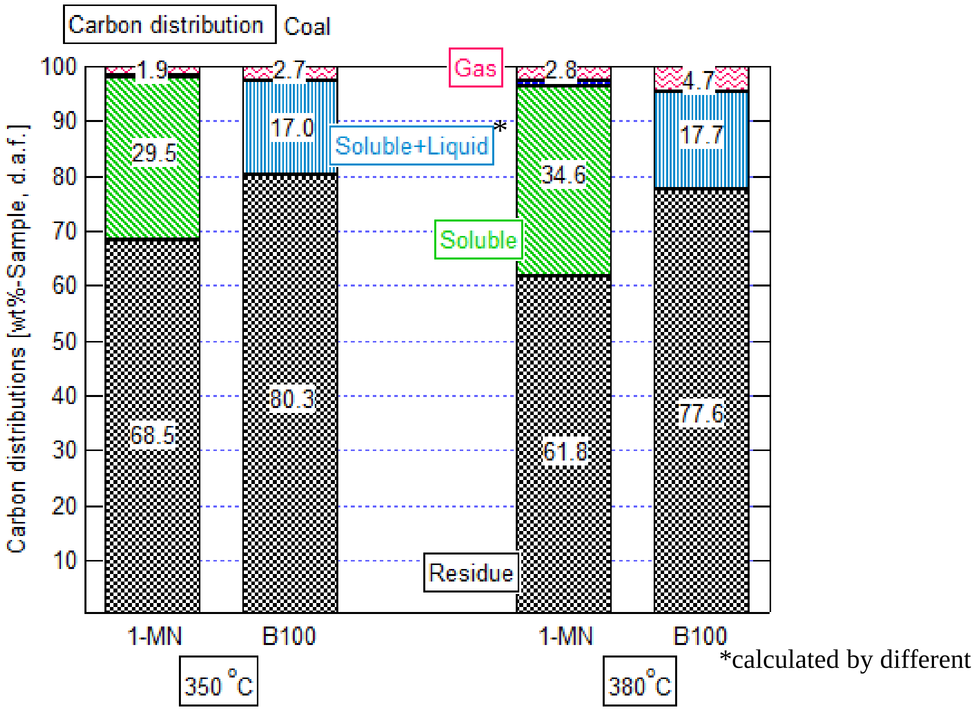
(a)



(b)



(c)

Figure 4.12 Carbon distributions to products from (a) Rice straw, (b) Leucaena and (c) coal by 1-MN and B100 solvents at 350 and 380 °C

3) Element Distributions to product from WS3060 solvent

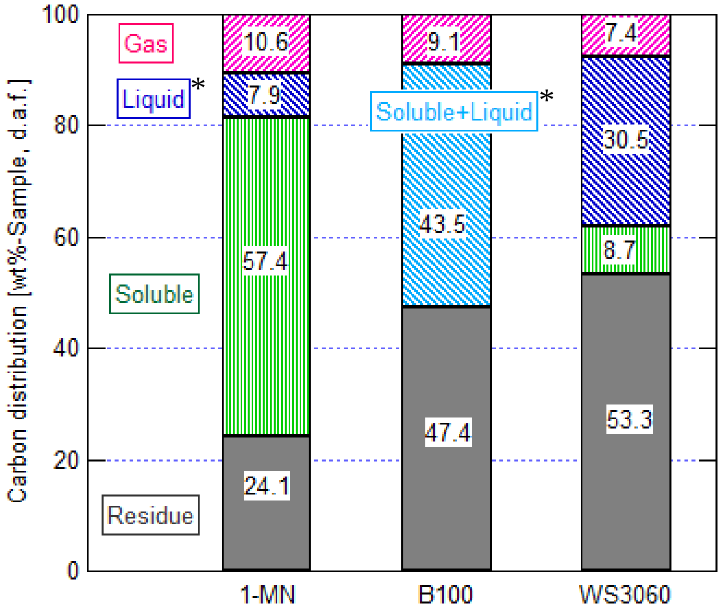
The molar distributions of the element to the product by using WS3060 solvent with RS, LC and coal at 350 °C were given in Table 4.9. For RS, the carbon was distributed to Soluble and Residue respectively by 8.7 %, and 53.3 %, indicating that 62.0 % of carbon was retained in the solid product. The hydrogen was distributed to the gaseous product, Liquid, Soluble and Residue respectively by 0.5 %, 66.2 %, 5.5 % and 27.8 %. For LC, the carbon was distributed to Soluble and Residue respectively by 10.5 % and 53.3 %, indicating that 63.8 % of carbon was retained in the solid product. The hydrogen was distributed to the gaseous product, Liquid, Soluble and Residue respectively by 0.9 %, 63.4 %, 8.4 % and 27.3 %. From the results, the element distributions to the products for both biomasses look similar when using WS3060 solvent. In total 82.5 to 88.4 % of oxygen were distributed to either gaseous product or Liquid for RS and LC, respectively. This means that more than 80 % of oxygen was removed as CO2, CO, and H2O at 350 °C.

The element distributions through the product from coal are shown in Figure 4.13. The carbon was distributed to Soluble and Residue respectively by 5.9 % and 92.4 %, indicating that 98.3 % of carbon was retained in the solid product. The hydrogen was distributed to the gaseous product, Liquid, Soluble and Residue respectively by 0.4 %, 22.4 %, 9.4 %, and 67.7 %.

The carbon based yields of RS, LC and coal from 1-MN, B100 and WS3060 at 350 °C are shown in Figure 4.13. The carbon based gaseous yields obtained from 1-MN, B100 and WS3060 were quite similar. The Soluble yields extracted from WS3060 solvent were very small when compared with 1-MN and B100 solvent. This was probably because the soluble product cannot dissolve in WS3060 and precipitated into solid form at room temperature. For the soluble fractions, the carbon recovered as Soluble by using WS3060 was lower than 1-MN solvent. This showed that using WS3060, the molecule of the extracted was smaller than those from 1-MN and became to Liquid product. These results indicated that B100 and WS3060 had a potential as a solvent for the degradative solvent extraction.

Table 4.9 Product yields, ultimate analyses, element distributions to products obtained from RS, LC and Coal at three temperatures using WS3060 solvent

Sample	Yield [wt%, d.a.f.]	Utimate Analysis [wt%, d.a.f.]				Proximate Analysis [wt%, d.b.]			Elemental Balance [mol/g, d.a.f.]		
		C	H	N	O*	VM	FC	Ash	C	H	O
Rice straw	-	47.0	6.5	0.6	45.9	67.5	15.9	16.6	39.2	65.0	28.7
Residue	35.0	71.6	5.2	1.0	22.3	37.1	29.9	33.0	20.9	18.1	4.9
Soluble	5.2	78.9	6.8	0.6	13.7	79.6	20.4	0.0	3.4	3.6	0.4
Gas	10.9	31.9	0.3	-	67.7				2.9	0.4	4.6
Liquid*	48.9								12.0	43.0	18.7
Leucaena		47.7	6.2	0.7	45.4	82.6	16.0	1.4			
Residue	34.8	73.0	4.9	1.2	21.0	44.1	52.9	2.9	21.2	16.9	4.6
Soluble	6.2	80.0	8.3	0.7	10.9	79.3	20.7	0.0	4.2	5.2	0.4
Gas	10.1	31.7	0.6	-	67.7				2.7	0.6	4.3
Liquid*	48.8								11.7	39.3	19.1
Coal		63.3	5.0	1.0	30.7	52.9	40.4	6.7	52.7	50.3	19.2
Residue	83.2	70.3	4.1	1.3	24.4	45.4	46.5	8.1	48.7	34.1	12.7
Soluble	4.6	80.8	10.3	0.4	8.6	91.6	8.4	0.0	3.1	4.8	0.2
Gas	2.4	30.1	0.8	-	69.1				0.6	0.2	1.0
Liquid*	9.8								0.3	11.3	5.2



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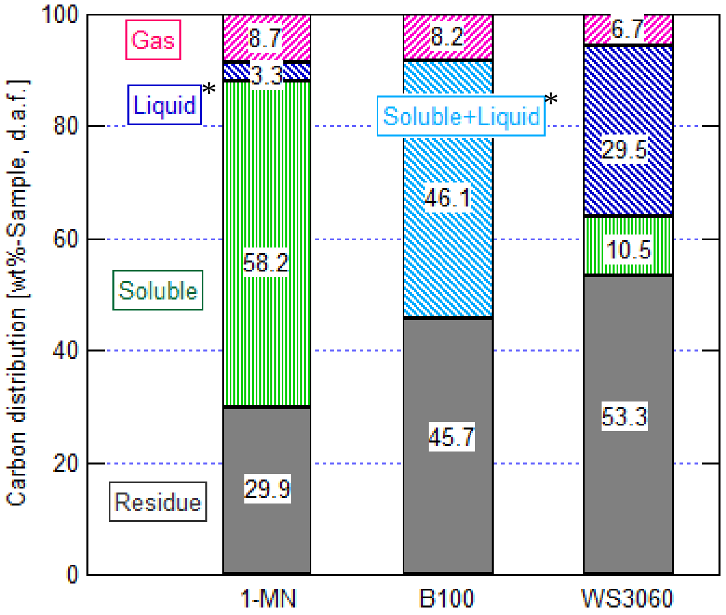
(a)



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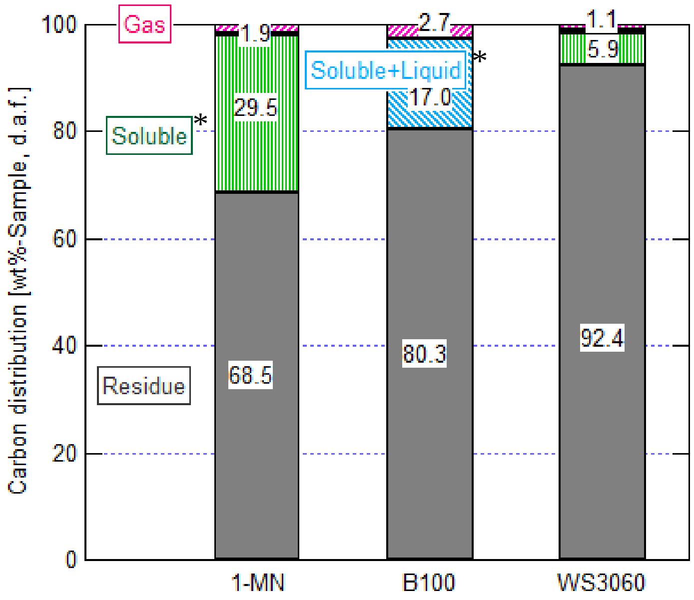


*calculated by different

(c)

Figure 4.13 Carbon distributions to products yields from (a) Rice straw, (b) Leucaena and (c) Coal by 1-MN, B100 and WS3060 solvents at 350 °C

4.4 Properties of solid products

4.4.1 Ash Contents of the Soluble products

When the products were utilized as fuel, the ash contents mattered. Tables 4.7-9 showed the proximate analyses of the solid products with those of coal and biomass samples. It was surprising to note that solubles from both 1-MN and WS3060 were completely free from ash. This means that almost all of ash was retained in residues.

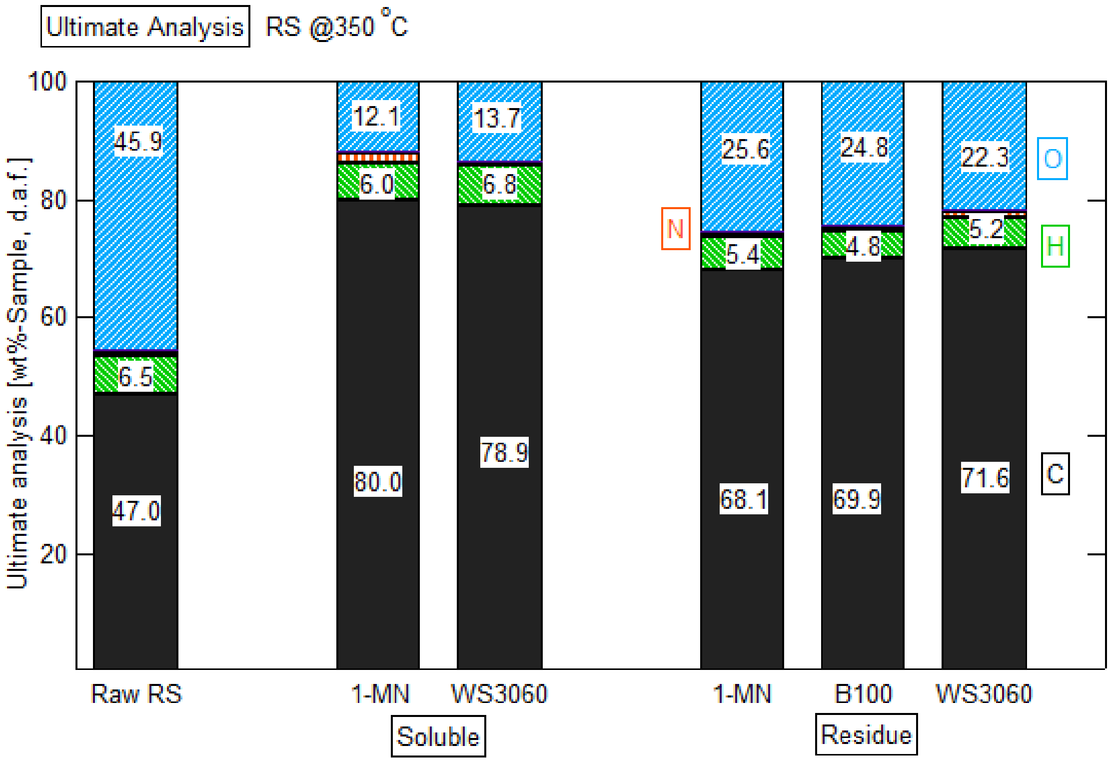
4.4.2 Elemental composition of the solid products

1) Compare the Elemental compositions of the solid products from 1-MN, B100 and WS3060

The elemental compositions of the solid products from RS, LC and coal using 1-MN, B100 and WS3060 solvents at 350 °C are shown in Figure 4.14. All of solid product, soluble and residue were analyzed by CHN analysis. It was found that the percent carbon contained in soluble from RS were very high as about 80.0 % and 78.9 % (wt%- d.a.f.) for 1-MN and WS3060, respectively. The percentages of oxygen were about 12.1 % and 13.7 % (wt%- d.a.f.), respectively for 1-MN and WS3060. The elemental composition of soluble from using 1-MN and WS3060 were very similar. The oxygen contain in soluble product was very low. For the elemental compositions in residue fraction, these show that the degradative solvent extraction method can upgrade biomass by using 1-MN, B100 and WS3060. The percentages of carbon were about 68.1 %, 69.9 % and 71.6 % (wt%- d.a.f.) for 1-MN, B100 and WS3060, respectively. The percentages of oxygen were about 25.6 %, 24.8 % and 22.3 % (wt%- d.a.f.) in the same order. The percentages of carbon of residue were high up while the oxygen contained in residues decrease when compare with raw RS. It can concluded that the elemental compositions of these soluble and residue from three solvents were quite similar.

Similar trends with RS, the percent carbon contained in soluble from LC was also very high as about 81.1 % and 80.0 % (wt%- d.a.f.) for 1-MN and WS3060, respectively. The percentages of oxygen were about 10.8 % and 10.9 % (wt%- d.a.f.), respectively for 1-MN and WS3060. The elemental composition of soluble from using 1-MN and WS3060 were very similar. The oxygen contain in soluble product was very low. For the elemental compositions in residue, the percentages of carbon were about 73.1 %, 68.9 % and 73.0 % (wt%- d.a.f.) for 1-MN, B100 and WS3060, respectively. The percentages of oxygen were about 20.0 %, 26.3 % and 21.0 % (wt%- d.a.f.) in the same order. The percentages of carbon increase and the oxygen contained in residues decrease when compared with raw LC. The elemental compositions of these soluble and residue from three solvents were quite similar. These results show that the biomass can be upgraded by B100 and WS3060 solvent. Although using WS3060 as solvent was obtained soluble product lower than 1-MN. The chemical property of soluble from 1-MN and WS3060 were very similar.

For coal, despite the raw materials having different properties from raw biomass, the chemical properties of the products from coal were not very different from biomass. The percent carbon contained in soluble from coal were also very high as about 79.8 % and 80.8 % (wt%- d.a.f.) for 1-MN and WS3060, respectively. The percentages of oxygen were about 12.0 % and 8.6 % (wt%- d.a.f.), respectively for 1-MN and WS3060. The elemental composition of soluble from using 1-MN and WS3060 were very similar. The oxygen contain in soluble product was very low. For the elemental compositions in residue fraction, these show that the degradative solvent extraction method can upgrade coal by using 1-MN, B100 and WS3060. The percentages of carbon were about 66.7 %, 64.6 % and 70.3 % (wt%- d.a.f.) for 1-MN, B100 and WS3060, respectively. The percentages of oxygen were about 27.9 %, 31.3 % and 24.4 % (wt%- d.a.f.) in the same order. The percentages of carbon increase when compare with raw coal. The elemental compositions of these soluble and residue from three solvents were quite similar. These results show that both coal and biomass can be upgraded and fractionated by the B100 and WS3060 solvents.



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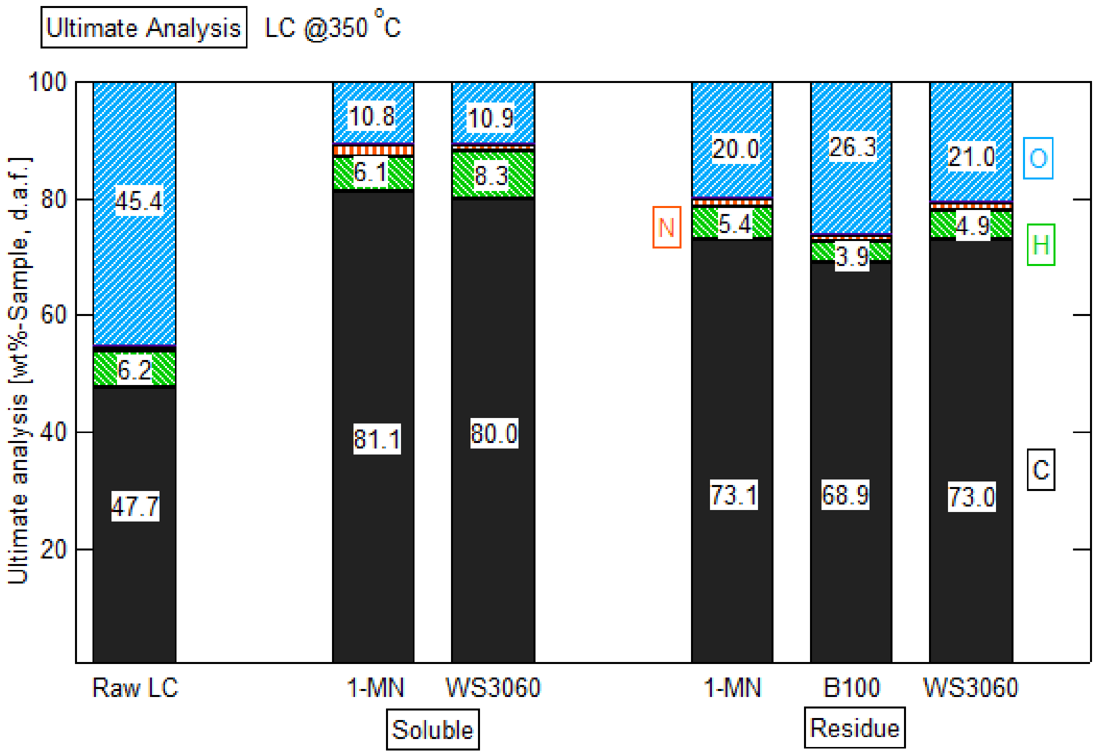

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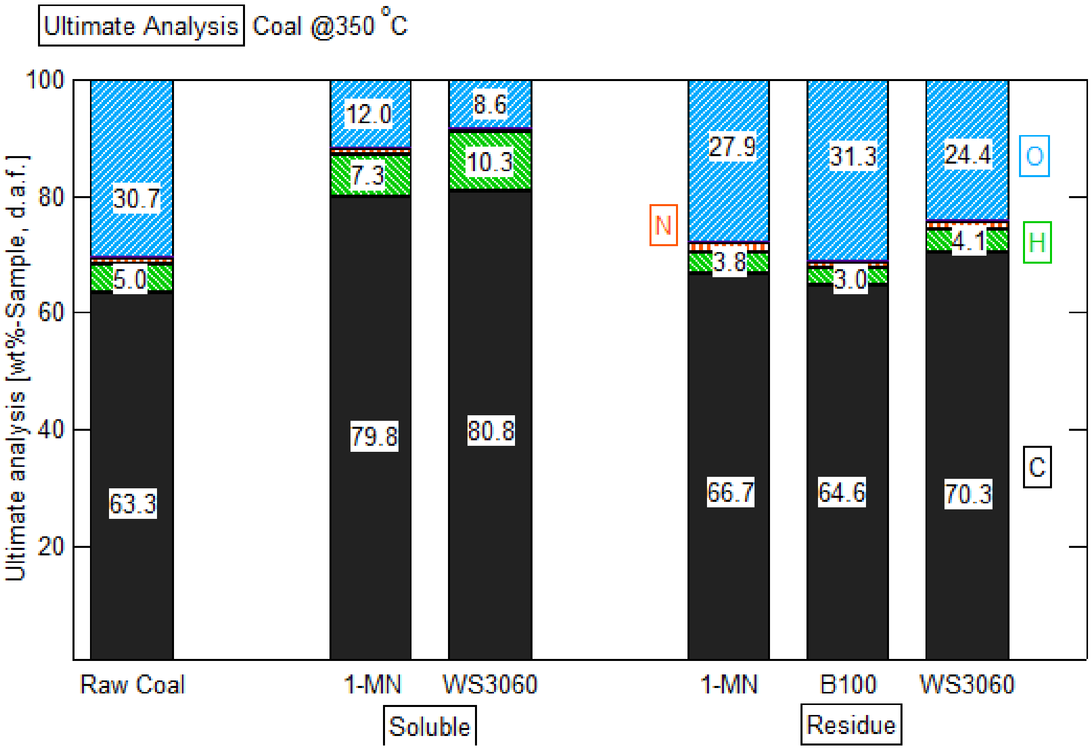


(c)

Figure 4.14 The elemental composition of solid products using 1-MN, B100 and WS3060 from (a) Rice straw, (b) Leucaena and (c) Coal

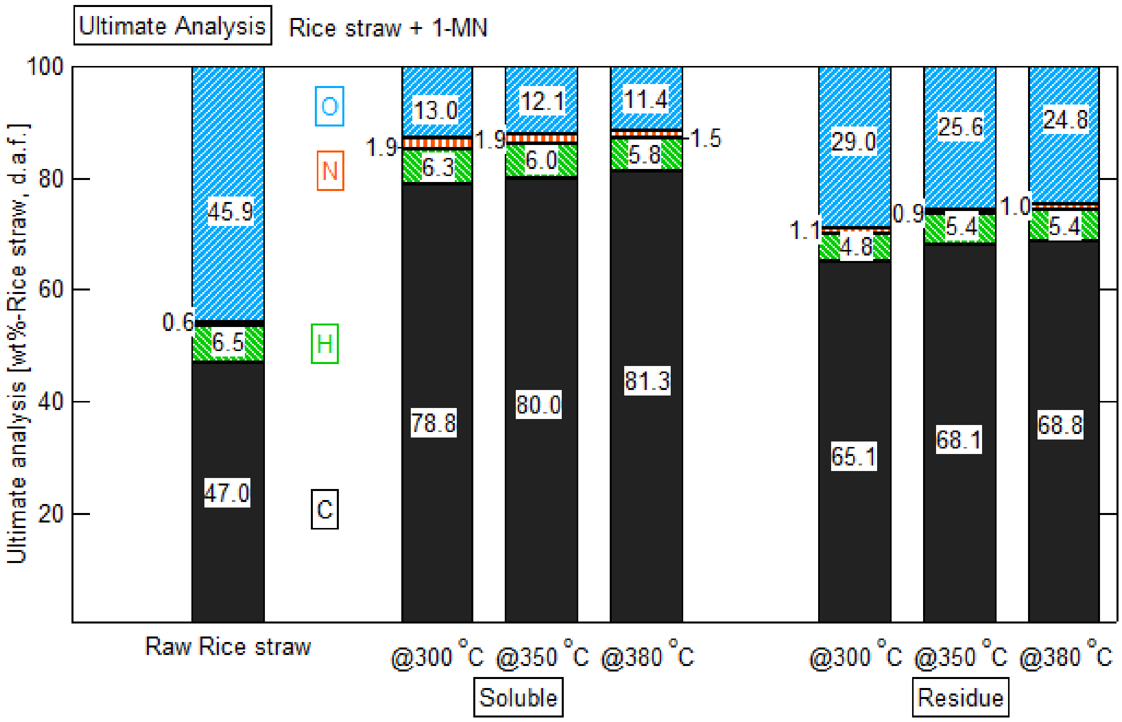
2) Elemental composition of solid products using 1-MN

The elemental compositions of the solid products from RS using 1-MN solvent are shown in Figure 4.15 (a). It was found that, the percent carbon in soluble was very high and depend on treatment temperature. The percentages of carbon were about 78.8 %, 80.0 % and 81.3 % (wt%- d.a.f.) at 300, 350 and 380 °C, respectively. This show that the percent carbon in soluble increased with increasing treatment temperature. The percentages of oxygen were about 13.0 %, 12.1 % and 11.4 % (wt%- d.a.f.) in the above order. The oxygen contain in soluble product was very low and decreased with increasing treatment temperature. For the residue products, the carbon contain were higher than raw RS at each temperature. The percentages of carbon were about 65.1 %, 68.1 % and 68.8 % (wt%- d.a.f.) at 300, 350 and 380 °C, respectively. The oxygen contain in residue product also decreased with increasing treatment temperature.

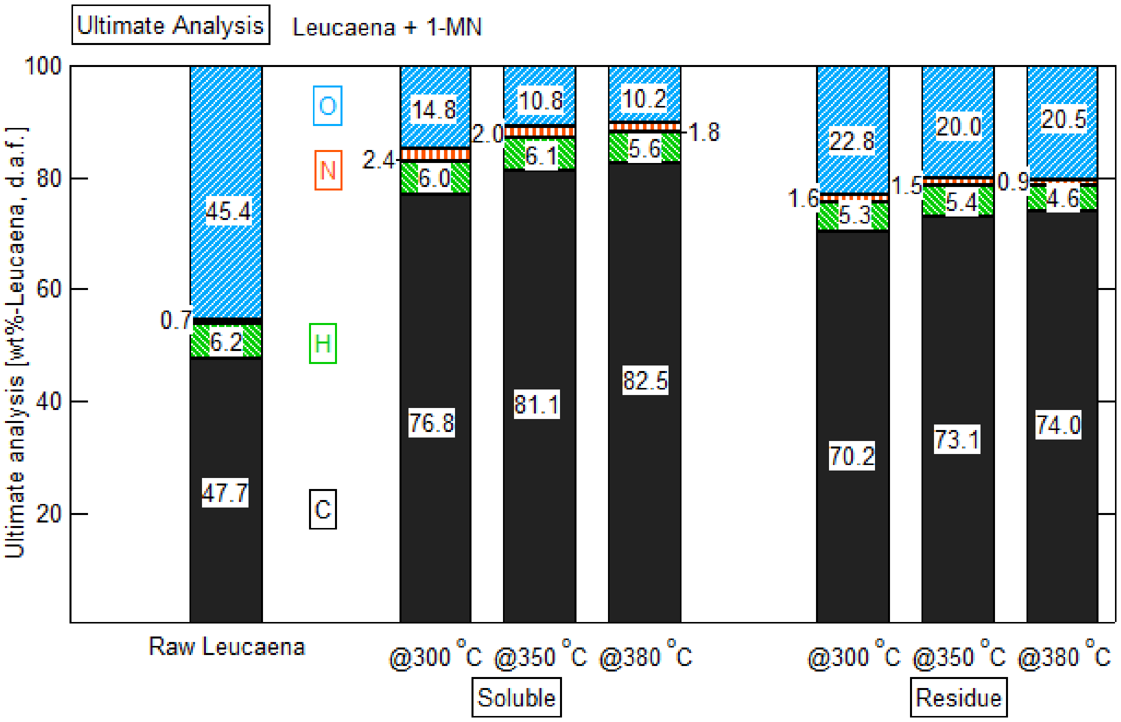
The elemental composition of the solid products from the LC and 1-MN solvent, were quite similar to RS. The results are shown in Figure 4.15 (b). The percent carbon in soluble was also very high and depend on treatment temperature. The percentages of carbon were about 76.8 %, 81.1 % and 82.5 % (wt%- d.a.f.) at 300, 350 and 380 °C, respectively. The percentages of oxygen were about 14.8 %, 10.8 % and 10.2 % (wt%- d.a.f.) in the above order. For the residue products, the carbon content was higher than raw LC at each temperature. The percentages of carbon were about 70.2 %, 73.1 % and 74.0 % (wt%- d.a.f.) at 300, 350 and 380 °C, respectively. For residue product from RS and LC, although the element composition in law LC and RS were quit similar, but the carbon contain in residue from residue from LC was higher than RS. This was probably because the different in the structural composition in each biomass.

For coal sample, there were similar changes with the biomasses. The results are shown in Figure 4.15 (c). The percentages of carbon in soluble were about 78.5 %, 79.8 % and 82.4 % (wt%- d.a.f.) at 300, 350 and 380 °C, respectively. The percentages of oxygen were about 13.0 %, 11.6 % and 9.6 % (wt%- d.a.f.) in the above order. For the residue products, the carbon contain (d.a.f.) were higher than raw Coal at each temperature. The percentages of carbon were about 66.1 %, 66.7 % and 70.4 % (wt%- d.a.f.) at 300, 350 and 380 °C, respectively.

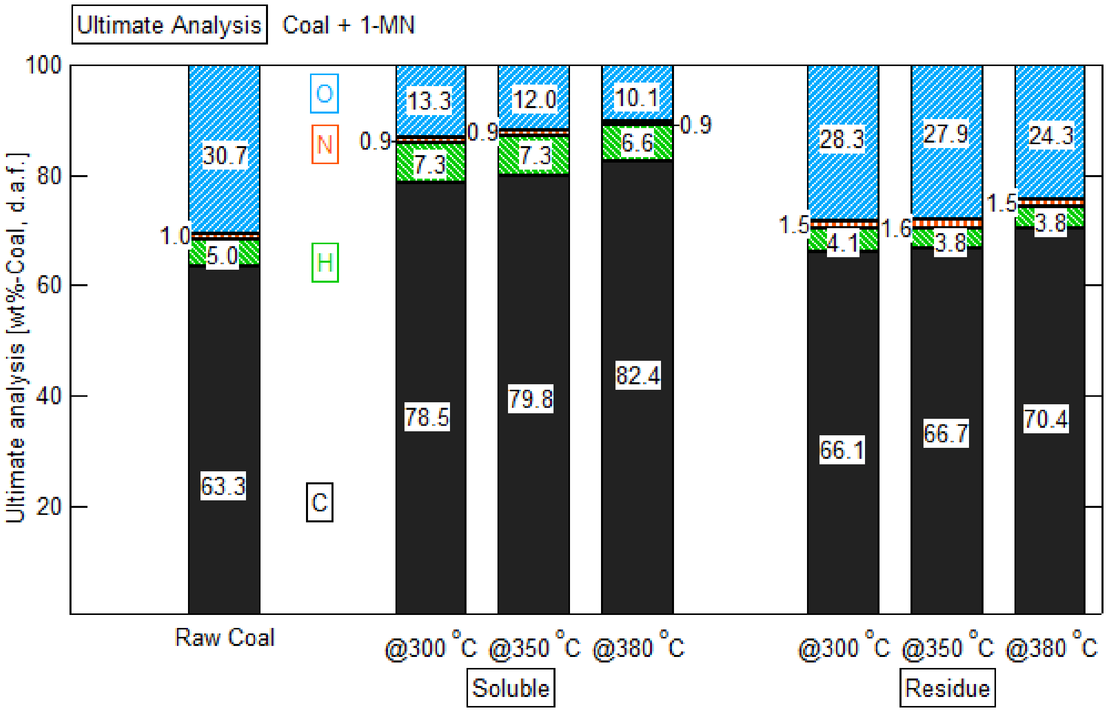
These results show that 1-MN can be used to extract the soluble product from biomass and coal into a high quality product. The soluble from coal and biomass were very high in percent carbon and not difference in term of element composition. From the element composition in residue product, it shown that coal and biomass can be upgraded by increase the carbon contain and decrease the percentages of oxygen in raw material.


Ultimate Analysis
Rice straw + 1-MN
100
80
60
40
20
Ultimate analysis [wt%-Rice straw, d.a.f.]
O
N
H
C
45.9
0.6
6.5
47.0
13.0
1.9
6.3
78.8
12.1
1.9
6.0
80.0
11.4
1.5
5.8
81.3
29.0
1.1
4.8
65.1
25.6
0.9
5.4
68.1
24.8
1.0
5.4
68.8
Raw Rice straw
@300 °C
@350 °C
@380 °C
Soluble
@300 °C
@350 °C
@380 °C
Residue

(a)


Ultimate Analysis
Leucaena + 1-MN
100
80
60
40
20
Ultimate analysis [wt%-Leucaena, d.a.f.]
O
N
H
C
45.4
0.7
6.2
47.7
14.8
2.4
6.0
76.8
10.8
2.0
6.1
81.1
10.2
1.8
5.6
82.5
22.8
1.6
5.3
70.2
20.0
1.5
5.4
73.1
20.5
0.9
4.6
74.0
Raw Leucaena
@300 °C
@350 °C
@380 °C
Soluble
@300 °C
@350 °C
@380 °C
Residue

(b)



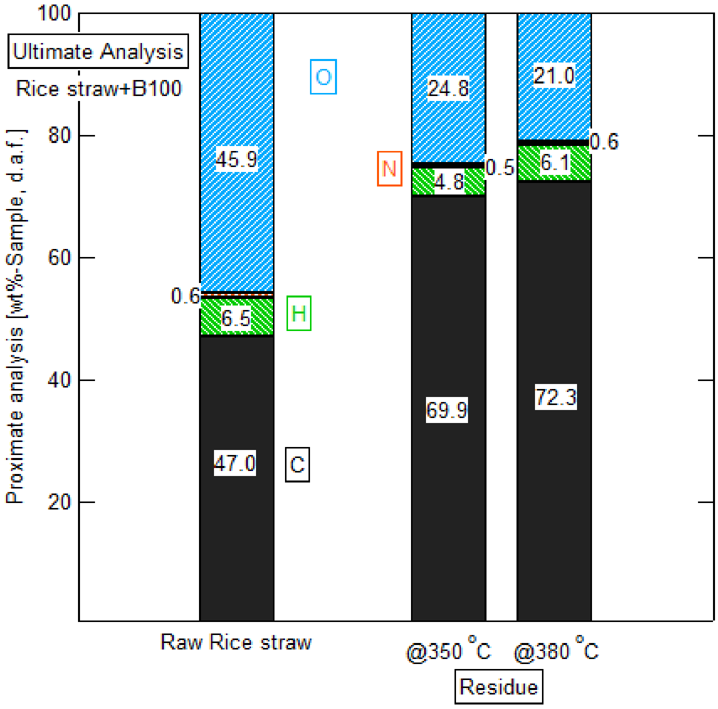
(c)

Figure 4.15 The elemental composition of solid products by 1-MN solvent with Rice straw (a), Leucaena (b) and Coal (c)

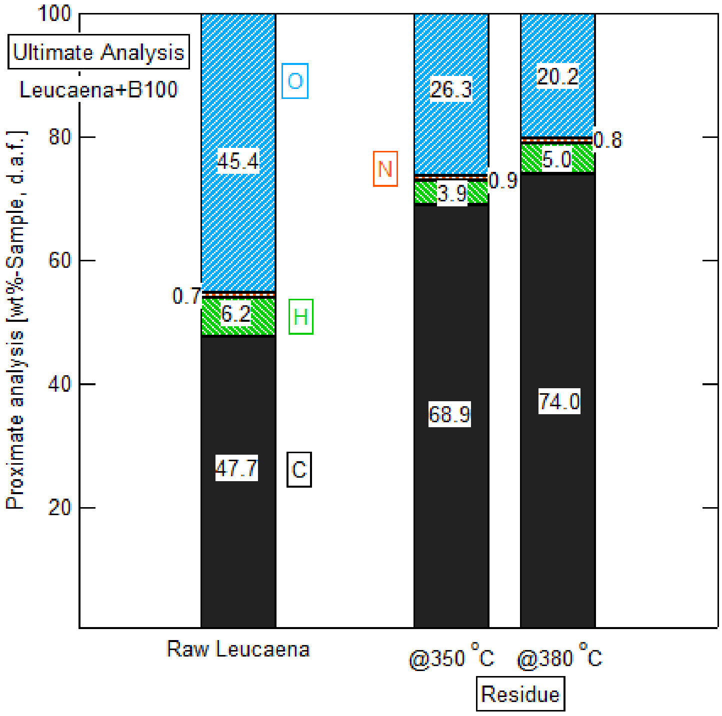
3) Elemental composition of solid product using B100

It was difficult to remove the solvent from the soluble fraction when we used B100 as a solvent. The elemental compositions in residue products from B100 solvent were examined for study the element distribution in next lesson. Elemental composition of the residue products from RS and B100 solvent are shown in Figure 4.16 (a). From the result, the carbon contain in the residue were higher than raw RS at each temperature. The percentages of carbon were about 69.9 % at 350 °C and increased to 72.3 % at 380 °C. The oxygen contained was about 24.8 % at 350 °C and decreased to 21.0 % at 380 °C. Figure 4.16 (b) showed the result from LC and B100 solvent. The percentages of carbon were about 68.9 % and 74.0 % (wt%- d.a.f.) at 350 °C and 380 °C, respectively. The oxygen contain were about in 26.3 % and 20.2 % (wt%- d.a.f.) in the order which decreased with increasing treatment temperature. For coal sample, the results are shown in Figure 4.16 (c). The percent carbon was about 64.6 % and 70.8 % (wt%- d.a.f.) at 350 °C and 380 °C, respectively. The oxygen content was about 31.3 % and 24.7 % (wt%- d.a.f.) in the order.

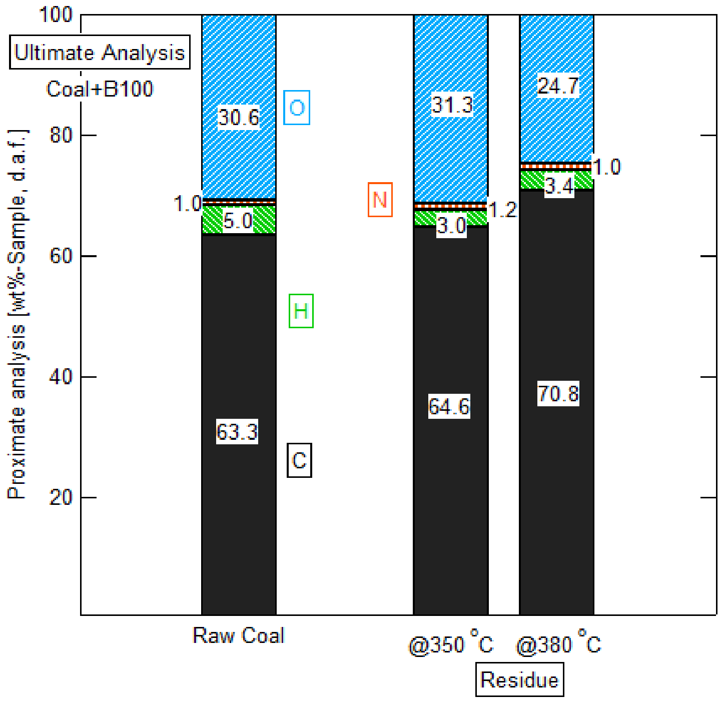
These results show that B100 can be used as solvent treatment for upgrading coal and biomass by increasing the carbon content and decreasing the percentages of oxygen in the raw material.



(a)



(b)



(c)

Figure 4.16 The elemental composition of solid products by B100 solvent with (a) Rice straw, (b) Leucaena and (c) Coal

CHAPTER 5

CONCLUSION

The degradative solvent extraction method was applied to upgrade and fractionate coal and biomass: Rice straw (RS) and Leucaena (LC) using 1-Methylnaphalene, Biodiesel from palm oil and WS3060 as the solvents. For 1-MN was very effective solvent when compared with B100 and WS3060. The carbon based yields of Soluble and Residue products which operated at 350 °C were as high as 57.4 % and 24.1 wt%, respectively for RS, and 58.2 % and 29.9 wt%, respectively for LC. The highest of the product yield from coal was operated at 380 °C. The carbon based yields of Soluble and Residue products which operated at 380 °C were as high as 34.6 % and 61.8 wt%, respectively. The solubles which extracted by 1-MN solvent were the largest yield fractions for biomass. Although the carbon based yields of soluble from coal was smaller than biomass, the carbon retained in solid product was high up to 96.4%.

For the B100 solvent, it was difficult to remove the solvent from the soluble fraction. So, the “Soluble + Liquid” fraction for B100 was quantified by the difference. The carbon-based yields of the “Soluble + Liquid” fraction from RS were 43.5 % and 45.3 % at 350 and 380 °C, respectively. The carbon-based yields of the “Soluble + Liquid” fraction from LC were 46.1 % and 51.7 % at 350 and 380 °C, respectively. The carbon-based yields of the “Soluble + Liquid” fraction from Coal were 17.0 % and 17.7 % at 350 and 380 °C, respectively. Although, it is difficult to remove the solvent from Soluble fraction when we used B100 as a solvent. It is suggested that B100 has a potential as a solvent for the degradative solvent extraction.

For the WS3060 solvent, the degradative solvent extraction method was examined by using this solvent at 350 °C. The carbon based yields of Soluble and Residue products which operated at 350 °C were as high as 8.7 %, and 53.3 wt%, respectively for RS, 10.5 % and 53.3 wt%, respectively for LC, and 5.9 % and 92.4 %wt%, respectively for Coal. The Soluble yields extracted from this solvent were very small when compared with 1-MN solvent and B100. Moreover the property of product using WS3060 (both soluble and residue) was similar to 1-MN. This is probably because the soluble product does not dissolve in WS3060 and precipitated into solid at room temperature. Although, the carbon recovered as Soluble by using WS3060 was smaller than using 1-MN solvent, this solvent can be used for the upgrading both of coal and biomass by removing the oxygen as CO_2, CO, and H2O.

Suggestion

It is difficult to remove the solvent from soluble fractions when using B100 as the solvent. Therefore, it is suggested to mix the soluble and the solvent into high quality liquid bio-fuel.

The hypothesis about the effect of the WS3060 on degradative solvent extraction needs an in-depth study. The WS3060 solvent itself also should be analyzed in order to understand the mechanism or the effect of this solvent on the degradative extraction.

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