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ผลลัพธ์ที่ได้จากโครงการ

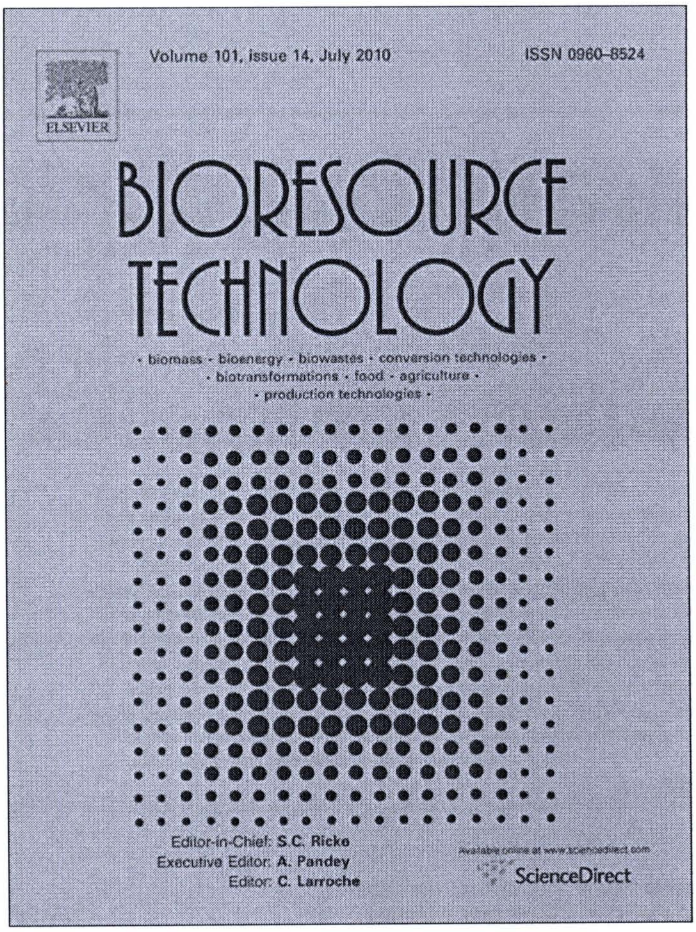
ผลงานวิจัยที่ตีพิมพ์ในวารสารวิชาการระดับนานาชาติ

1) Wongsiriamnuay, T., Tippayawong, N., 2010. Non-isothermal pyrolysis characteristics of giant sensitive plants using thermogravimetric analysis. *Bioresource Technology*, 101, 5638-5644.
2) Wongsiriamnuay, T., Tippayawong, N., 2010. Thermogravimetric analysis of giant sensitive plants under air atmosphere. *Bioresource Technology*, 101, 9314-9320.
3) Tippayawong, N., Inthasan, P., 2010. Investigation of light tar cracking in a gliding arc plasma system. *International Journal of Chemical Reactor Engineering,* 8, A50.

ผลงานที่นำเสนอในที่ประชุมวิชาการ

1) Wongsiriamnuay, T., Tippayawong, N., Phengpom, T., Panthong, P., 2008. Renewable energy from thermal gasification of a giant sensitive plant (Mimosa pigra L.). *5th International Conference on Combustion, Incineration/Pyrolysis and Emission Control*, Chiang Mai, Thailand, December 6-19.
2) Thiha, S., Tippayawong, N., Wongsiriamnuay, T., Chaichana, C., 2009. Catalytic destruction of biomass tar by dolomite in a dual packed bed reactor. *2nd International Conference on Green and Sustainable Innovation*, Chiang Rai, Thailand, December 2-4.
3) Wongsiriamnuay, T., Tippayawong, N., 2010. Gasification of giant sensitive plants in a fixed bed reactor. *23rd International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems*, Lausanne, Switzerland, June 14-17.

ภาคผนวก



Volume 101, issue 14, July 2010
ISSN 0960-8524
ELSEVIER

BIORESOURCE
TECHNOLOGY

· biomass · bioenergy · biowastes · conversion technologies ·
· biotransformations · food · agriculture ·
· production technologies ·

Editor-in-Chief: S.C. Ricke
Executive Editor: A. Pandey
Editor: C. Larroche
Available online at www.sciencedirect.com
ScienceDirect

Bioresource Technology 101 (2010) 5638–5644

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Non-isothermal pyrolysis characteristics of giant sensitive plants using thermogravimetric analysis

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ARTICLE INFO

Article history:
Received 23 December 2009
Received in revised form 5 February 2010
Accepted 8 February 2010
Available online 1 March 2010

Keywords:
Biomass
Mimosa
Pyrolysis
Renewable energy
Thermal decomposition

ABSTRACT

A giant sensitive plant (*Mimosa pigra* L.) or Mimosa is a fast growing woody weed that poses a major environmental problem in agricultural and wet land areas. It may have potential to be used as a renewable energy source. In this work, thermal behaviour of dried Mimosa was investigated under inert atmosphere in a thermogravimetric analyzer at the heating rates of 10, 30, and 50 °C/min from room temperature to 1000 °C. Pyrolysis kinetic parameters in terms of apparent activation energy and pre-exponential factor were determined. Two stages of major mass loss occurred during the thermal decomposition process, corresponding to degradation of cellulose and hemicellulose between 200–375 °C and decomposition of lignin around 375–700 °C. The weed mainly devolatilized around 200–400 °C, with total volatile yield of about 60%. The char in final residue was about 20%. Mass loss and mass loss rates were strongly affected by heating rate. It was found that an increase in heating rate resulted in a shift of thermograms to higher temperatures. As the heating rates increased, average devolatilization rates were observed to increase while the activation energy decreased.

1. Introduction

Future contribution of renewable energy is vital as energy becomes increasingly scarce and expensive. Use of diverse biomass resources is projected to contribute to a major fraction of future energy demands. Nonetheless, competition between biomass supply for fuel or for food applications has been intensified in the recent years. This concern has resulted in growing interests in alternative, non-edible biomass resources such as perennial rhizomatous grasses; miscanthus (*Miscanthus*), switchgrass (*Panicum virgatum*), reed canary grass (*Phalaris arundinacea*), giant reed (*Arundo donax*) and bamboo because of their high yield potential, appropriate biomass characteristics, low input demand and positive environmental impact (Lewandowski et al., 2003; Basso et al., 2005; Scurlock et al., 2000). In Thailand, non-plantation biomass resources have been assessed for their energy potential and found to be promising (Sujjakulnukit et al., 2005). Weeds such as giant sensitive plants are viewed to have potential as an useful bioenergy source. Giant sensitive plant is woody member of the genus Mimosa, in the family Fabaceae comprising about 400–450 species. It is a woody invasive shrub that originates from tropical America. Now, it can be found in tropical and subtropical areas over many countries especially Australia, Thailand, Vietnam, South American, and African countries. It forms dense, thorny impenetrable thickets, particularly in wet areas. It is one of the worst environmental weeds. Owing to its strong, dense and woody stems, some small fraction of Mimosa is utilised as firewood, bean-poles, and as temporary fences. So far, there have been relatively few literatures reporting on utilisation of Mimosa as feedstock for bioenergy (Presnell, 2004; Wongsiriamnuay et al., 2008).

Thermal conversion technology is an attractive route to produce fuel gases from natural resources. When the thermal process is carried out in a reactor, the raw material undergoes pyrolysis, gasification and combustion. They are complicated processes consisting of several main chemical reactions and large number of intermediate reactions. Many alternative paths are available to the reacting compounds, depending on the process conditions. Physico-chemical compositions of the fuel are also important and decisive factors for the characteristics of the thermal conversion. Thermogravimetric analysis (TGA) can be an useful tool to study the thermal behaviour of materials. The rate of mass loss as a function of temperature and time is measured and provides a means to estimate the kinetic parameters in the thermal decomposition reaction. These data are crucial for efficient modeling, design and operation of pyrolysis process and related thermochemical conversion systems. To determine the effect of temperature and heating rate on their pyrolysis characteristics, the samples are pyrolyzed under non-isothermal conditions in a thermogravimetric analyzer. Many TGA studies have been carried out for pyrolysis of various non-edible biomass sources (Jeguirim and Trouve, 2009; Park et al., 2009; Kumar et al., 2008; Maiti et al., 2007; Erlich et al., 2006; Collura et al.,

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doi:10.1016/j.biortech.2010.02.037

2005; Cao et al., 2004; Meszaros et al., 2004; Fisher et al., 2003; Müller-Hagedorn et al., 2003; Gronli et al., 2002; Karaosmanoglu et al., 2001). To the authors' knowledge, there has not yet been a report on pyrolysis characteristics of giant sensitive plants. The objectives of this investigation are therefore to study pyrolysis characteristics and to analyze change of kinetic behaviour with conversion for the giant sensitive plant. Comparisons are made against other biomass sources.

2. Methods

2.1. Samples

The samples of Mimosa collected in agricultural zone in Chiang Mai, Thailand were used. The collected stalks were cleaned and air dried naturally in a dry store room at ambient condition. The dried samples were crushed and grounded in a high speed rotary mill, and sieved to provide a feed sample in the size range of about 0.5 mm. Preparation of samples prior to analyses was conducted in accordance with TAPPI T 257 and T 264 standards. Contents of the major biopolymer constituents of the weed, holocellulose, lignin and solvent extractive components were evaluated using TAPPI standard methods. The solubilities of extractives in ethanol and benzene mixture as well as quantity of soluble substances in sodium hydroxide and in water were established. ASTM standard methods were followed to carry out proximate analysis for the samples. The carbon, hydrogen and nitrogen contents were determined using a CHN elemental analyzer. The oxygen content was calculated by difference. The heating value of the dried Mimosa stalk was determined in compliance with ASTM standard using a Parr bomb calorimeter. It was reported as a gross heat of combustion at constant volume. Analysis results of the dried Mimosa samples are shown in Table 1.

2.2. Thermogravimetric apparatus

Thermal decomposition of the biomass materials were analyzed using a TGA/SDTA 851e thermogravimetric analyzer (sensitive microbalance, 1 μg resolution, 1300 °C maximum temperature at atmospheric pressure, 50 bar maximum at 1000 °C, and 30 °C/min maximum heating rate). This high performance TG analyzer has high sensitivity, vibration resistance and structure that permit rapid replacement of samples. Large number of samples can be analyzed in a short time and in succession. The system was logged to a personal computer for data handling and analysis. Prior to TGA, temperature, weight and sample platform calibrations were carried out. Each sample was placed in the platinum pan securely and in such a way that it was confined within the pan sides and not in contact with the sides of the oven. All handling of samples were done using brass tweezers to avoid contamination. Non-isothermal experiment runs were carried out at 10, 30, and 50 °C/min under atmospheric pressure, with an initial weight sample of 5 mg and a purge gas flow of 50 cm^3/min. The purge gases used were high purity nitrogen, air or oxygen. The sample was initially preheated to and equilibrated at 40 °C in nitrogen under a flow rate of 50 cm^3/min for 10 min. The sample was then heated to 1000 °C at a constant heating rate. The continuous records of weight loss and temperatures were obtained. At least three runs were performed for each condition.

Table 1
Analysis of dried Mimosa samples.

Property	Unit	Method	Quantity
Proximate analysis			
Moisture	(% w/w)	ASTM D 3173	1.6
Volatile	(% w/w)	ASTM D 3175	71.1
Fixed carbon	(% w/w)	ASTM D 3172	23.6
Ash	(% w/w)	ASTM D 3177	3.7
Ultimate analysis			
Carbon	(%)	ASTM D 3174	43.9
Hydrogen	(%)	ASTM D 3174	6.0
Nitrogen	(%)	ASTM D 3174	1.4
Oxygen	(%)	By difference	48.7
Lignocellulosic content			
Holocellulose	(% w/w)	Wise method	58.2
Lignin	(% w/w)	TAPPI T 222	33.9
Higher heating value	(MJ/kg)	ASTM 5865	17.5

3. Results and discussion

3.1. Thermal decomposition

The proximate chemical compositions of Mimosa stems were found to be similar to hard woods, but with higher ash content (Nordin, 1994). Ultimate analysis showed that raw Mimosa consisted of moderately high carbon content (43.9%) and low amounts of hydrogen (6.0%) and nitrogen (1.4%). Cellulose and hemicellulose were presented in terms of holocellulose, accounting for nearly 60% of total mass. Lignin content of Mimosa was found to be relatively high (33.9%). During pyrolysis of lignocellulosic materials, mass losses occurred due to dehydration at low temperatures, decomposition of hemicellulose, cellulose and lignin. Decompositions of these components were normally overlapped (Jeguirim and Trouve, 2009).

Thermal decomposition behaviours of Mimosa pyrolysis under flowing nitrogen were obtained. The results of thermogravimetric experiments were expressed as conversion α, defined as:

$$\alpha = \frac{W_i - W_t}{W_i - W_f} \tag{1}$$

where W_i, W_t and W_f are the initial mass of the sample, the mass of pyrolyzed sample, and the final residual mass, respectively. The degree of conversion versus temperature at different heating rates of 10, 30 and 50 °C/min for the giant sensitive plant in TG analyzer are shown in Fig. 1. At the temperature lower than 150 °C, the small change of conversion in the samples was attributed to vaporisation of moisture that was attached on the surface of the samples. The giant sensitive plant samples started to decompose and release volatile matter around 200 °C. The TG curves of the giant sensitive trees showed only two major weight loss stages between 200 and 400 °C, and 400 and 700 °C. It was clear that the slope of the curve changed between the two temperature intervals. Slope between 200 and 400 °C was higher than that 400 and 700 °C. The conversions at different heating rates exhibited similar patterns. It was observed at temperatures below 400 °C that the TG curve shifted slightly to the right with increasing heating rate. At low heating rates, several distinct mass loss zones observed were associated with degradation dynamics of main constituents. Since the samples contained mainly cellulose, hemicellulose and lignin, it was known that the hemicellulose started to decompose at around 225–325 °C and the cellulose was found to decompose between 325 and 375 °C. Lignin had a broad decomposition temperature range at temperatures higher than 250–500 °C (Shafizadeh, 1985; Di Blasi and Lanzetta, 1997; Ferdous et al., 2002). As the heating rate was increased, these thermal degradation zones tended to merge. Simultaneous participation of all components cannot be avoided in measured mass loss (Di Blasi, 2008). Decomposition at 500 °C or higher progressed slowly due to the remaining lignin or char, similar to that reported by Fisher et al. (2003).

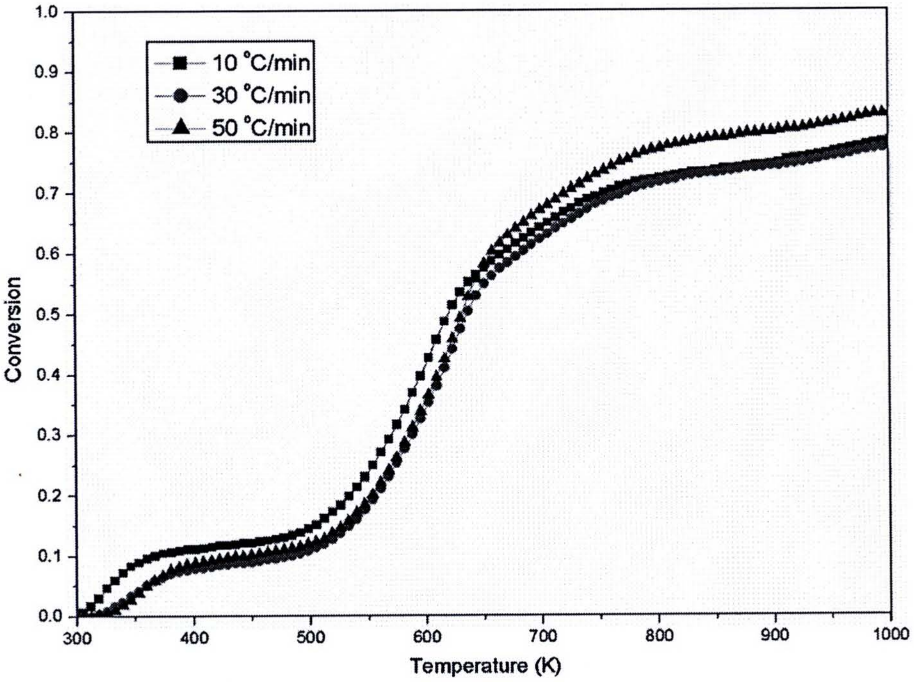

Fig. 1. Conversion as a function of temperature in the thermal treatment of Mimosa under nitrogen atmosphere at different heating rates.

The differential rates of instantaneous conversion, $d\alpha/dt$, were obtained from TG analysis at different heating rates, shown in Fig. 2. The differential TG curve of each heating rate has one extensive peak, occurred between 325 and 375 °C. The maximum peaks were attributed to the decomposition of cellulose and hemicellulose. Higher heating rate was found to shift the differential TG curve to a greater range of temperature. This was attributed to the fact that when the heating rate was increased, the retention time was shorter and the temperature required for organic matter to decompose was greater (Ferdous et al., 2002; Senneca, 2007; Jeguirim and Trouve, 2009), causing the maximum curve rate to move rightward. These behaviours were similar to those reported by Wang et al. (2008) and Jeguirim and Trouve (2009). Increasing the heating rate also led to an increase in the maximum rate of $d\alpha/dt$ of the TG curve (Ferdous et al., 2002; Hu et al., 2007). The maximum points of the

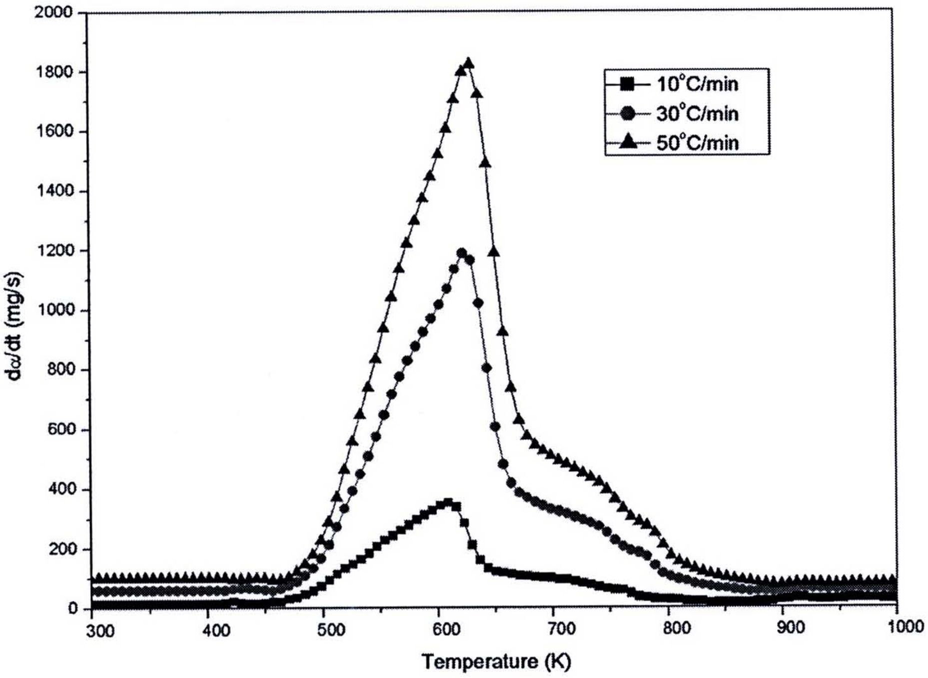

Fig. 2. DTG curves of thermal decomposition of Mimosa under nitrogen at different heating rates.

Table 2
Degradation characteristic of various biomass sources at low heating rates.

Reference	Biomass	T_{start} (°C)	T_{peak} (°C)	$d\alpha/dt_{peak}$	α_{peak}	$\alpha_{500°C}$	Heating rate (°C/min)
This work	Mimosa	198	336	0.748	0.45	0.29	10
		191	350	2.33	0.42	0.30	30
		197	356	4.11	0.49	0.24	50
Gronli et al. (2002)	Alder	242	349	1.02	0.40	0.17	5
	Beech	248	349	0.91	0.37	0.18	5
	Birch	244	353	0.98	0.32	0.14	5
	Oak	237	338	0.89	0.45	0.23	5
	Douglas fir	243	334	0.87	0.55	0.24	5
	Pine A	238	351	0.91	0.45	0.20	5
	Pine B	209	350	0.81	0.43	0.20	5
	Redwood	235	351	0.83	0.50	0.26	5
	Spruce	249	352	0.77	0.46	0.23	5
	Hard woods	243	347	0.95	0.38	0.18	5
	Soft woods	235	348	0.84	0.47	0.22	5
Kalita and Saikia (2004)	*P. alba*	170	360	–	0.58	–	20
	C. procera	210	290	–	0.85	–	20
	E. neerifolia	180	360	–	0.76	–	20
	N. indicum	140	350	–	0.68	–	20
	M. elengi	170	340	–	0.57	–	20
Gomez et al. (2007)	Thistle	214	334	0.20	–	–	20
	Pine	254	378	0.30	–	–	20
	Beech	259	380	0.35	–	–	20
Yao et al. (2008)	Bagasse	–	299.3	–	0.53	–	2
	Bamboo	–	285.9	–	0.44	–	2
	Cotton stalk	–	293.4	–	0.50	–	2
	Hemp	–	282.3	–	0.38	–	2
	Jute	–	283.1	–	0.44	–	2
	Kenaf	–	284.1	–	0.42	–	2
	Rice husk	–	297.4	–	0.37	–	2
	Rice straw	–	273.6	–	0.35	–	2
	Maple	–	308.3	–	0.58	–	2
	Pine	–	311.5	–	0.59	–	2
Jeguirim and Trouve (2009)	Giant reed	200	308	0.826	0.58	0.29	5

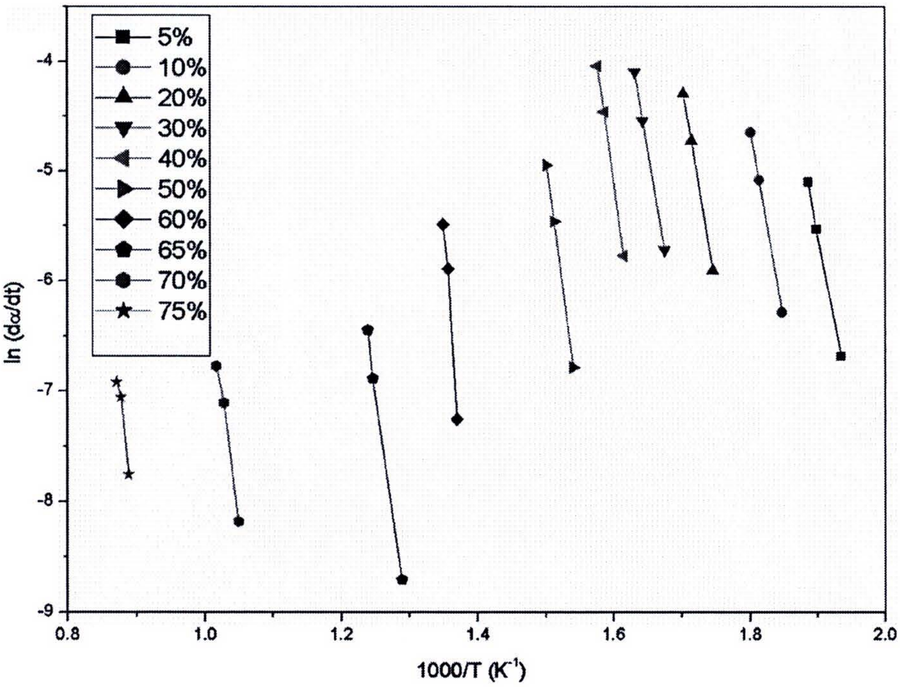

Fig. 3. Relationships between the rate of conversion with temperature for conversions of 5–75%.

TG curves occurred at 335, 350 and 355 °C for heating rates of 10, 30 and 50 °C/min, respectively. It can be seen that the maximum rate of decomposition tended to increase at higher heating rate because it provided higher thermal energy to facilitate better heat transfer between the surrounding and inside the samples. These results were in similar trends with previous re-

Table 3
Comparison of calculated pyrolysis kinetic parameters between Mimosa and other biomass resources.

References	Biomass		*n*	Conversion (%)											
				5	10	15	20	30	40	50	60	65	70	75	80
This work	Mimosa	E (kJ/mol)		269.32	293.10	–	311.50	306.43	373.91	370.46	364.57	371.22	366.38	410.93	403.72
		A	0th	2.08×10^{24}	3.65×10^{25}	–	6.81×10^{25}	2.10×10^{24}	1.10×10^{29}	7.16×10^{26}	1.94×10^{23}	1.58×10^{21}	3.49×10^{16}	5.25×10^{15}	5.72×10^{11}
			1st	4.16×10^{23}	3.65×10^{24}	–	3.40×10^{24}	6.99×10^{22}	2.74×10^{27}	1.43×10^{25}	3.24×10^{21}	2.43×10^{19}	4.98×10^{14}	7.00×10^{13}	7.15×10^{9}
			2nd	8.32×10^{22}	3.65×10^{23}	–	1.70×10^{23}	2.33×10^{21}	6.85×10^{25}	2.86×10^{23}	5.40×10^{19}	3.74×10^{17}	7.11×10^{12}	9.33×10^{11}	8.94×10^{7}
Park et al. (2008)	Japanese larch	E (kJ/mol)		220	–	–	–	–	–	–	–	–	–	–	1009
		A	0th	5.24×10^{17}	8.57×10^{16}	–	3.35×10^{16}	3.57×10^{15}	5.11×10^{15}	1.36×10^{14}	8.41×10^{12}	–	1.61×10^{13}	–	5.78×10^{14}
			1st	1.05×10^{19}	8.57×10^{17}	–	1.67×10^{17}	1.19×10^{16}	1.28×10^{16}	2.71×10^{14}	1.40×10^{13}	–	2.30×10^{13}	–	7.22×10^{14}
			2nd	2.10×10^{20}	8.57×10^{18}	–	8.37×10^{17}	3.96×10^{16}	3.19×10^{16}	5.42×10^{14}	2.34×10^{13}	–	3.29×10^{13}	–	9.03×10^{14}
Park et al. (2009a)	Oriental white oak	E (kJ/mol)		166	–	–	–	–	–	–	–	–	230	–	777
		A	0th	1.81×10^{12}	3.05×10^{13}	–	1.16×10^{15}	7.60×10^{15}	3.82×10^{16}	4.02×10^{15}	2.51×10^{14}	–	1.42×10^{14}	–	2.37×10^{19}
			1st	3.62×10^{13}	3.05×10^{14}	–	5.81×10^{15}	2.53×10^{16}	9.56×10^{16}	8.04×10^{15}	4.19×10^{14}	–	2.03×10^{14}	–	2.97×10^{19}
			2nd	7.25×10^{14}	3.05×10^{15}	–	2.90×10^{16}	8.44×10^{16}	2.39×10^{17}	1.61×10^{16}	6.98×10^{14}	–	2.90×10^{14}	–	3.71×10^{19}
Park et al. (2009b)	Oak tree	E (kJ/mol)		245.79	238.28	–	241.61	254.73	247.81	227.07	216.39	–	217.92	–	384.34
		A	0th	3.13×10^{21}	6.46×10^{19}	–	1.65×10^{19}	4.61×10^{19}	3.01×10^{18}	2.12×10^{16}	1.51×10^{15}	–	8.63×10^{14}	–	5.79×10^{26}
			1st	6.26×10^{22}	6.46×10^{20}	–	8.25×10^{19}	1.54×10^{20}	7.53×10^{18}	4.23×10^{16}	2.52×10^{15}	–	1.23×10^{15}	–	7.24×10^{26}
			2nd	1.25×10^{24}	6.46×10^{21}	–	4.13×10^{20}	5.13×10^{20}	1.88×10^{19}	8.46×10^{16}	4.20×10^{15}	–	1.76×10^{15}	–	9.05×10^{26}
Wang et al. (2008)	Sawdust	E (kJ/mol)		–	–	202.3	185.8	177.3	172.0	164.6	164.4	164.6	163.5	161.9	166.4
		A	0th	–	–	4.8×10^{5}	4.5×10^{13}	2.0×10^{12}	2.7×10^{11}	2.9×10^{10}	1.6×10^{10}	1.3×10^{10}	8.4×10^{9}	5.0×10^{9}	9.5×10^{9}
	Cellulose	E (kJ/mol)		–	–	167.7	163.0	159.2	154.3	151.4	148.8	149.0	148.4	146.0	142.6
		A	0th	–	–	2.8×10^{11}	8.2×10^{10}	2.6×10^{10}	7.6×10^{9}	3.4×10^{9}	1.7×10^{9}	1.6×10^{9}	1.3×10^{9}	7.1×10^{8}	3.2×10^{8}
	Hemicellulose	E (kJ/mol)		–	–	250.1	194.8	163.0	158.2	158.7	168.5	170.4	175.1	196.3	228.0
		A	0th	–	–	3.4×10^{22}	1.6×10^{16}	4.3×10^{12}	7.6×10^{11}	5.2×10^{11}	2.9×10^{12}	3.4×10^{12}	7.6×10^{12}	5.1×10^{14}	2.1×10^{17}
	Lignin	E (kJ/mol)		–	–	162.3	154.8	133.8	157.8	186.8	195.4	194.8	189.0	183.1	157.7
		A	0th	–	–	7.6×10^{11}	6.7×10^{10}	1.1×10^{8}	5.8×10^{8}	2.3×10^{10}	4.7×10^{10}	3.2×10^{10}	9.2×10^{9}	2.6×10^{9}	2.5×10^{7}

ports (Park et al., 2009b; Jeguirim and Trouve, 2009; Kumar et al., 2008).

Table 2 presents comparison of degradation characteristics in terms of onset temperature from the decomposition of hemicellulose component (T_{start}), maximum conversion (α_{peak}), maximum mass loss rate ($d\alpha/dt_{peak}$) and its corresponding temperature (T_{peak}), and percentage char yield at 500 °C ($\alpha_{500°C}$) between Mimosa and other biomass sources (Jeguirim and Trouve, 2009). Decomposition of Mimosa's hemicellulose component was at similar temperature (~200 °C) to giant reed and latex bearing plants, but lower than wood species. It was clear that the thermal degradation of Mimosa under inert atmosphere occurred at similar temperatures to those obtained for latex plant samples at similar TGA conditions (Kalita and Saikia, 2004). The maximum mass loss rate was obtained at similar range (340–360 °C) to other wood and latex plant samples (Gronli et al., 2002; Kalita and Saikia, 2004; Gomez et al., 2007), but slightly higher than agro-residues (Yao et al., 2008). Peak mass loss rate of Mimosa at 10 °C/min heating rate was in similar magnitude to giant reed and wood samples at 5 °C/min. However, if thermal degradation of wood residues at 20 °C/min was considered (Gomez et al., 2007), the Mimosa mass loss rate at 10 and 30 °C/min was found to be higher. Mimosa appeared to exhibit similar maximum conversion to wood and agro-residues, in the range between 0.32 and 0.59.

3.2. Kinetic parameters

The kinetic parameters for the global pyrolysis process of Mimosa can be calculated using similar procedure adopted by Park et al. (2009b) and Maiti et al. (2007). The general non-isothermal, decomposition reaction rate is;

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \qquad (2)$$

where

$$k = A\exp(-E/RT) \qquad (3)$$

T is the temperature, A is the pre-exponential or frequency factor, t is the time, E is the activation energy, R is the universal gas constant, n is the order of reaction. The logarithmic form for Eq. (3) is

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n\ln\alpha - \frac{E}{RT} \qquad (4)$$

Activation energy can be determined from the relationship between $\ln(d\alpha/dt)$ and $1/T$. Fig. 3 shows the relationship between $\ln(d\alpha/dt)$ and $1/T$ at various conversions from 5% to 75%. Thus, a family of parallel straight lines with a slope of $-E/R$ is obtained. When the heating rate was of 10, 30 and 50 °C/min, for example, the 10% conversion was obtained at the temperature of 267.4, 279.3 and 282.4 °C, respectively. At these temperatures, the values of $\ln(d\alpha/dt)$ were −6.28, −5.08 and −4.65, respectively. From the slope of $\ln(d\alpha/dt)$ against $1/T$ at the conversion of 10%, the activation energy was calculated as 293.10 kJ/mol. The intercept ($\ln(A\cdot\alpha^n)$) can also be obtained from Fig. 3, at each conversion. When the apparent order of reaction is assumed to be 0th, 1st or 2nd, the pre-exponential or frequency factor can be obtained from the following equation

$$\ln(A\alpha^n) = \ln A + n\ln\alpha \qquad (5)$$

The variation of activation energy as a function of the conversion level, calculated using Eq. (5) is presented in Table 3. The activation energy for the pyrolysis of Mimosa ranged from 269 to 411 kJ/mol, depending on the conversion. The activation energy was found to increase from the conversion of 5% up to 40%, and appeared to remain relatively stable at an average value of 370 kJ/mol for the conversion between 40% and 70%. When the conversion increased from 70% to 80%, the activation energy increased sharply. This observed behaviour may be due to an influence of heat or mass transfer at high temperatures greater than 500 °C. The activation energy values obtained here were higher than those obtained from oak tree, saw dust, and woods (Park et al., 2009b; Wang et al., 2008; Müller-Hagedorn et al., 2003), except for larch and white oak at high conversion (Park et al., 2008, 2009a). Jeguirim and Trouve (2009) reported the activation energies for cellulose and hemicelluloses to be in the range of 90–140 and 110 kJ/mol while Wang et al. (2008) reported the range of 142–168 and 158–250 kJ/mol for cellulose and hemicelluloses, respectively. The increase of activation energy at higher conversion may be attributable to further devolatilization of char after the main reaction. Most of cellulose and hemicelluloses were decomposed at the pyrolytic conversion from 5% to 70% with the average activation energy of 330 kJ/mol.

Also shown in Table 3 are the calculated pre-exponential factors, assuming the reaction order as zeroth, first or second. Main decomposition occurred at the conversion from 20% to 65%, where the pre-exponential factors were in the range of 10^{17}–10^{29} s^{-1}. When the conversion increased above 65%, the pre-exponential factors declined rapidly to 10^{7}–10^{16} s^{-1}, probably attributed to greater presence of residual char. These values were much larger than those reported for main decomposition of other biomass sources. Park et al. (2008, 2009a,b) calculated the pre-exponential factors for conversion between 20% and 70% to be in the range of 10^{13}–10^{20} s^{-1}, for larch, white oak and oak tree. Wang et al. (2008) reported even lower values for sawdust (10^{9}–10^{13} s^{-1}).

4. Conclusion

Thermal degradation of Mimosa under inert environment was investigated using TGA at different heating rates. Apparent activation energy and pre-exponential factor were determined. Pyrolysis of Mimosa occurred at similar temperatures to giant reed and latex bearing plants, but at lower temperatures than wood samples, between 200 and 500 °C. Increasing heating rate was found to increase mass loss rates but delay thermal decomposition to higher temperatures. The activation energy and pre-exponential factor were 269–411 kJ/mol, and 10^{7}–10^{29} s^{-1}, respectively. During pyrolysis, the kinetic parameters changed with conversion between 5% and 80%. This may be heat or mass transfer limitations at high temperatures.

Acknowledgements

This research is financially supported by the Thailand Research Fund (Contract No. RSA5080010) and Faculty of Engineering, Chiang Mai University. The Royal Golden Jubilee PhD scholarship (PHD/0047/2550) awarded to TW is greatly appreciated. Supports from the Energy Research and Development Institute, Chiang Mai University are also acknowledged.

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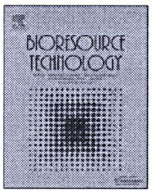
Bioresource Technology 101 (2010) 9314–9320

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech



Thermogravimetric analysis of giant sensitive plants under air atmosphere

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A R T I C L E I N F O

Article history:
Received 7 May 2010
Received in revised form 23 June 2010
Accepted 25 June 2010
Available online 23 July 2010

Keywords:
Biomass
Mimosa
Oxidation
Renewable energy
Thermal decomposition

A B S T R A C T

The aim of this work is to utilise thermal analysis to study the thermal degradation of giant sensitive plants (*Mimosa pigra* L.) or Mimosa under oxidative environment. Thermogravimetric method was used under air sweeping in dynamic conditions at the heating rates of 10, 30, and 50 °C/min, from room temperature to about 725 °C. Starting with dehydration step between 30 and 150 °C, the main thermal decomposition process under air showed two distinct degradation zones, corresponding to devolatilisation step between 200 and 375 °C and combustion step around 375–500 °C. Kinetic parameters in terms of apparent activation energy and pre-exponential factor were determined. Comparison was made against other biomass materials. Mass loss and mass loss rates were strongly affected by heating rate. It was found that an increase in heating rate resulted in a shift of thermograms to higher temperatures. As the heating rates increased, average devolatilisation and combustion rates were observed to increase while the activation energy showed slight increase.

1. Introduction

Biomass is a source of short-cycle carbon which is of utmost importance for the future energy. Common sources of biomass include woods, agricultural crops and residues. There have been growing interests in alternative, non-edible biomass resources such as fast growing tress; birch, poplar, willow, eucalyptus, and perennial rhizomatous grasses; miscanthus, switchgrass, reed canary grass, giant reed because of their high yield potential, appropriate biomass characteristics, low input demand and positive environmental impact (Berndes et al., 2003; Lewandowski et al., 2003). Apart from these dedicated energy crops, weeds can also be utilised. In tropical and subtropical areas over many countries especially Australia, Thailand, Viet Nam, South American, and African countries, giant sensitive plants (*Mimosa pigra* L.) or Mimosa are plentiful, and may be considered to be a useful, non-plantation biomass resource (Wongsiriamnuay and Tippayawong, 2010). So far, there have been relatively few studies on utilisation of Mimosa as feedstock for bioenergy.

Thermal conversion technology such as pyrolysis, gasification and combustion is an attractive route to produce fuel gases from natural resources. Combustion of biomass fuels occur when the volatile gaseous products from the thermal degradation ignite in the surrounding air. The heat released from combustion causes the ignition of adjacent unburned fuels. Analysis of the thermal degradation of biomass fuels is decisive in combustion and fire research for both fundamental and practical investigation. This has motivated a number of experimental investigations, usually based on thermogravimetric analysis (TGA). TGA is useful in studying the thermal behaviour of potential fuels. The rate of mass loss as a function of temperature and time is measured and provides a means to estimate the kinetic parameters in the thermal decomposition reaction. Most reported studies on biomass thermal decomposition focused on pyrolysis. Di Blasi (2008) gave a good review about the chemical and physical process modeling of wood and biomass pyrolysis under inert atmospheres. Decomposition of biomass under inert and oxidative atmospheres are influenced by different factors. Recently, a growing amount of TGA studies on thermal degradation of various non-edible biomass sources in oxidative environments have been carried out (Munir et al., 2009; Jeguirim et al., 2010; Sung and Seo, 2009; Yu et al., 2009; Ross et al., 2008; Haykiri-Acma and Yaman, 2008; Leroy et al., 2006; Garcia-Ibanez et al., 2006; Basso et al., 2005; Collura et al., 2005; Meszaros et al., 2004; Safi et al., 2004). However, there has been relatively little information on thermal behaviour of giant sensitive plants (Wongsiriamnuay and Tippayawong, 2010). Studies concerning the thermal degradation characteristics and kinetics of the weed under oxidizing environment were even less. In this study, thermal oxidative degradation characteristics of Mimosa were investigated. Thermal degradation rate in different steps was examined. Kinetic parameters were extracted. Change of kinetic behaviour with conversion was also analyzed. The kinetics of this thermal degradation is more closely related to combustion process. The work will therefore contribute to the development of efficient combustion applications for the giant sensitive plant.

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0960-8524/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2010.06.141

2. Methods

2.1. Samples

The samples of Mimosa were collected from an agricultural zone in Chiang Mai, Thailand. The preparation and analysis methods of the Mimosa samples can be found in the previous study (Wongsiriamnuay and Tippayawong, 2010). Contents of the major constituents of the weed from proximate and ultimate analyses for the samples, as well as the heating value of the Mimosa are shown in Table 1, in comparison to other biomass materials. The proximate chemical compositions of Mimosa stems were found to be similar to hard woods, with higher ash content than woods but lower ash content than other agro-residues. Ultimate analysis showed that raw Mimosa consisted of moderately high carbon content (43.9%) and low amounts of hydrogen (6.0%) and nitrogen (1.4%).

2.2. Thermogravimetric apparatus

Thermal decomposition of the biomass materials were analyzed using a TGA/SDTA 851e Thermogravimetric Analyser (sensitive microbalance, 1 µg resolution, 1300 °C maximum temperature at atmospheric pressure, 50 bar maximum at 1000 °C). This high performance TG analyser has high sensitivity, vibration resistance and structure that permit rapid replacement of samples. The system is logged to a personal computer for data handling and analysis. Prior to TGA, temperature, weight, and sample platform calibrations were carried out. Each sample was placed in the platinum pan securely and in such a way that it was confined within the pan sides and not in contact with the sides of the oven. All handling of samples were done using brass tweezers to avoid contamination. Non-isothermal experiment runs were carried out at 10, 30, and 50 °C/min under atmospheric pressure, with an initial weight sample of 5 mg and a purge gas flow of 50 cm^3/min. The purge gases used were high purity nitrogen, air or oxygen. The sample was initially preheated to and equilibrated at 40 °C in air under a flow rate of 50 cm^3/min for 10 min. The sample was then heated to 1000 °C at a constant heating rate. The continuous records of weight loss and temperatures were obtained. At least three runs were performed for each condition.

2.3. Reaction kinetics

Kinetics of non-thermal thermogravimetric behaviour were analyzed to determine apparent activation energy and pre-exponential factor for the Mimosa thermal degradation.

Thermal decomposition behaviours of Mimosa under flowing air were obtained. The results of thermogravimetric experiments were expressed as conversion α, defined as:

$$\alpha = \frac{W_i - W_t}{W_i - W_f} \tag{1}$$

where W_i, W_t and W_f are the initial mass of the sample, the mass of oxidized sample, and the final residual mass, respectively. The kinetic parameters for the global thermal degradation process of Mimosa can be calculated using similar procedure adopted by Wongsiriamnuay and Tippayawong (2010). The general non-isothermal, decomposition reaction rate is:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2}$$

where

$$k = A\exp(-E/RT) \tag{3}$$

T is the temperature, A is the pre-exponential or frequency factor, t is the time, E is the activation energy, R is the universal gas constant, n is the order of reaction. The logarithmic form for Eq. (2) is:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n\ln\alpha - \frac{E}{RT} \tag{4}$$

Activation energy can be determined from the relationship between $\ln(d\alpha/dt)$ and $1/T$.

When the apparent order of reaction is assumed to be 0th, 1st or 2nd, the pre-exponential or frequency factor can be obtained from the following equation:

$$\ln(A\alpha^n) = \ln A + n\ln\alpha \tag{5}$$

3. Results and discussion

TGA in air represents burning profiles and indicates a complex degradation route for the giant sensitive plant. The degree of conversion versus temperature at different heating rates of 10, 30 and 50 °C/min for Mimosa is shown in Fig. 1. The differential rates of instantaneous conversion, $d\alpha/dt$, were obtained from TG analysis at different heating rates, shown in Fig. 2. During thermal degradation in air, weight loss occurred continuously until the weight became almost constant. It can be seen that an initial weight loss of the samples was due to a loss of moisture starting at around 30 °C and continuing up to about 140 °C. The giant sensitive plant samples started to decompose and release volatiles at around 200 °C. The TG curves of the giant sensitive trees clearly showed changes

Table 1
Properties of Mimosa and other biomass materials.

Reference	Biomass	Proximate analysis (% w/w)				Ultimate analysis (%)				Heating value (MJ/kg)
		Moisture	Volatile	Fixed carbon	Ash	C	H	N	O	
This work	Mimosa	1.6	71.1	23.6	3.7	43.9	6.0	1.4	48.7	17.5 (HHV)
Haykiri-Acma and Yaman (2008)	Rapeseed	8.4	70	15.8	5.8	41.1	6.0	5.1	47.8	19.4 (HHV)
Kumar et al. (2008)	Corn stove	–	8.2	17.0	74.9	47.4	5.01	0.8	38.1	18.4 (HHV)
Munir et al. (2009)	Cotton stalk	–	76.1	18.8	5.1	47.1	4.6	42.1	1.2	17.4 (HHV)
	Sugar cane Bagasse	–	81.5	13.3	5.2	43.8	6.0	43.4	1.7	17.7 (HHV)
	Shea meal	–	66.3	28.7	5.0	48.6	5.9	37.7	2.9	19.8 (HHV)
Jeguirim et al. (2010)	Arundo donax	8.2	68.4	18.4	5.0	42.7	7.5	8.0	48.7	17.2 (HHV)
	Miscanthus	10.0	78.8	9.5	2.7	43.7	5.7	1.1	44.8	17.8 (HHV)
Shen et al. (2009)	Pine	12.9	71.5	15.3	0.3	41.9	4.5	0.2	40.2	16.8 (LHV)
	Aspens	8.2	80.4	11.0	0.4	45.8	5.2	0.4	39.9	18.8 (LHV)
	Birch	11.4	74.4	13.5	0.8	44.4	3.5	0.3	36.7	15.5 (LHV)
	Oak	8.8	76.8	14.2	0.2	45.4	5.0	0.3	41.3	18.9 (LHV)
Sun et al. (2010)	Cotton stalk	15	63.1	19.2	2.7	40.4	5.1	0.2	36.5	13.5 (LHV)
Otero et al. (2010)	Sewage sludge	6.8	59.2	8.4	32.4	55.3	7.8	9.7	25.6	16.5 (HHV)
	Animal manure	6.9	70.3	16.0	13.7	49.9	6.4	3.5	38.8	17.8 (HHV)
Safi et al. (2004)	Pine needle	–	74.2	24.1	1.7	45.8	5.4	1.0	46.1	18.5 (LHV)

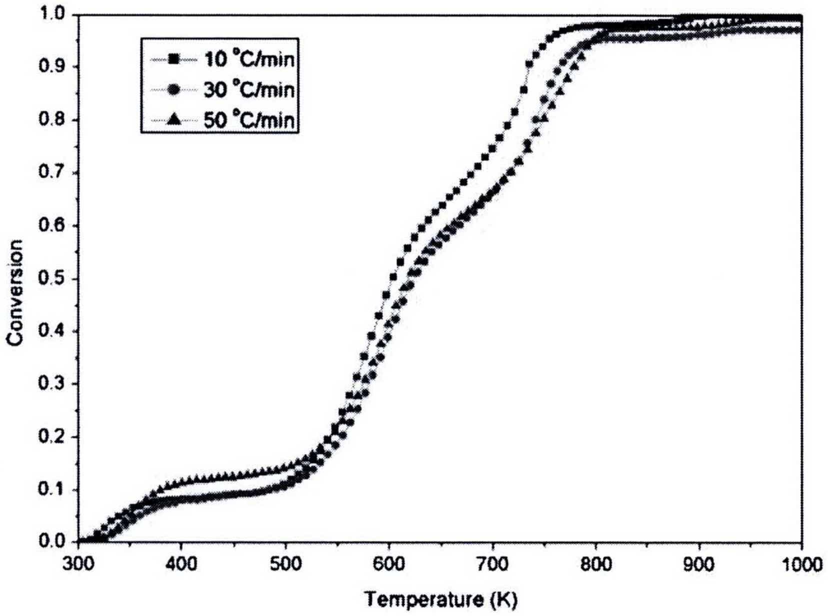

Fig. 1. Conversion as a function of temperature in the thermal degradation of Mimosa under air atmosphere at different heating rates.

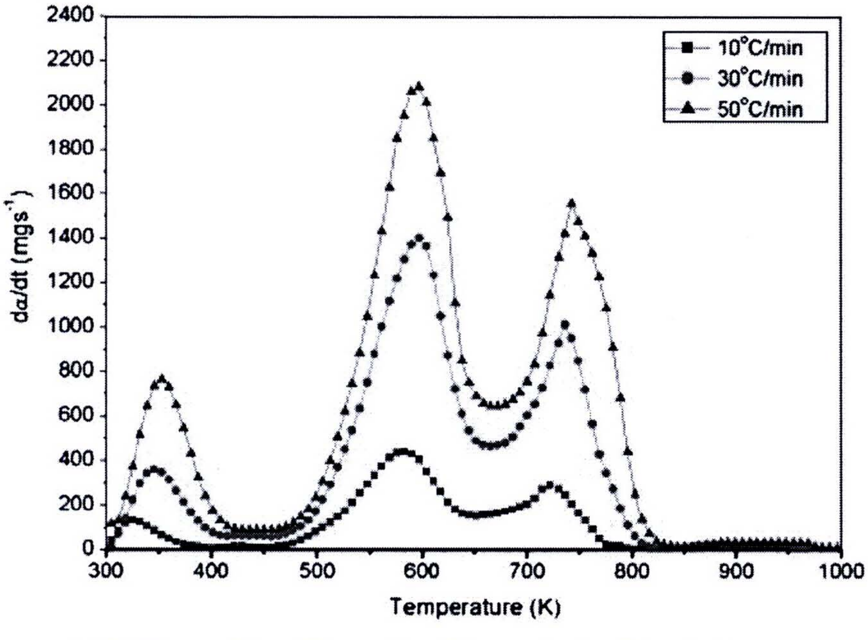

Fig. 2. DTG curves of thermal decomposition of Mimosa under air at different heating rates.

in the slope of the curve. The conversions at different heating rates exhibited similar patterns. It was observed at temperatures above 250 °C that the TG curve shifted slightly to the right with increasing heating rate. It was clear that the DTG curve of each heating rate exhibited two extensive peaks, occurred between 200 and 400 °C, and between 400 and 550 °C. From the TG curves, these two zones accounted for about 40% and 45% of total weight loss, respectively. The first stage was due to oxidative degradation and release of volatiles, while the second stage was due to char combustion. An overlapping between these regions was also apparent. The interpretation of TG results was along the similar line to Bilbao et al. (1997) and Fang et al. (2006) in which the first stage may be attributed to the devolatilisation of cellulose, hemicellulose, and lignin while the second stage may be due to the combustion of remaining char formed after the first stage. Safi et al. (2004) gave similar explanations that the first stage was caused by the total decomposition of cellulose and hemicellulose and partial decomposition of lignin while the second stage was due to the decomposition of remaining lignin and the combustion of char. Jeguirim et al. (2010) suggested that the second stage of mass loss was attributed to the fast combustion of readily combustibles and the slow oxidation of the not readily combustible part. The results observed here were in similar agreement with Shen et al. (2009). The TG results obtained under oxidative conditions were different from the pyrolysis of Mimosa (Wongsiriamnuay and Tippayawong, 2010), showing higher reaction rates. For a fixed heating rate, the weight loss stage due to oxidative pyrolysis was at higher rate than that observed from the pyrolysis of Mimosa in nitrogen atmosphere. Average rate of weight loss was so fast so that it reached maximum value at a lower temperature than that in an inert atmosphere. The presence of oxygen appeared to enhance decomposition of Mimosa at low temperature and promote the combustion of char residue. Higher heating rate was found to shift the DTG curve to a slightly greater range of temperature. This was attributed to the fact that increase in heating rate resulted in a reduction of the retention time, hence accelerating the evolution of volatiles. At higher heating rates, more reactions may be triggered simultaneously, leading to a rise in reaction rates and unstable radicals or intermediates. The DTG curves also showed consistently higher peaks with higher heating rates, shown in Table 2. The first and second peaks of the DTG curves occurred at 329, 460, 360, 480 and 374, 502 °C for heating rates of 10, 30 and 50 °C/min, respectively. It may be explained that thermal decomposition under high heating rate was affected by the rate of heat transfer inside the biomass materials as a result of the steep temperature gradient between the biomass particles and the surrounding. The maximum rate of decomposition tended to increase at higher heating rate because it provided higher thermal energy to facilitate better heat transfer between the surrounding and inside the samples. These results were in similar trends with previous reports (Kumar et al., 2008). This led the process of thermal decomposition to be delayed and the peaks of the DTG curves shifted towards higher temperatures. These behaviours were similar to those reported by Jeguirim et al. (2010). Also shown in Table 2 is the comparison of degradation characteristics in terms of maximum mass loss rate ($d\alpha/dT_{peak}$) and its corresponding temperature (T_{peak}) between Mimosa and other biomass sources. Degradation of Mimosa was at similar peak temperatures (~310 and 450 °C) for the first and second stages to wood species at the same heating rate of 10 °C/min (Shen et al., 2009), but higher than energy plants and agro-residues (Jeguirim et al., 2010; Munir et al., 2009; Safi et al., 2004). At higher heating rate, peak temperatures for thermal decomposition of Mimosa were found to be higher than woods, energy plants and agro-residues. It was also apparent that the maximum mass loss rates for the thermal degradation of Mimosa under air atmosphere were generally lower than other plant samples, both during devolatilisa-

Table 2
Comparison of degradation characteristic of various biomass materials.

Reference	Biomass	T_1 (°C)	$d\alpha_1/dT$ (%/C)	T_2 (°C)	$d\alpha_2/dT$ (%/C)	Heating rate (°C/min)
This work	Mimosa	310	0.26	448	0.19	10
		326	0.28	469	0.19	30
		326	0.25	469	0.20	50
Jeguirim et al. (2010)	Arundo donax	250	–	337	–	5
	Miscanthus	289	–	401	–	5
Munir et al. (2009)	Cotton stalk	285	0.28	373	0.12	20
	Bagasse	306	0.19	378	0.11	20
	Shea meal	279	0.21	442	0.14	20
Shen et al. (2009)	Pine	329	1.13	443	0.55	10
	Aspens	321	1.23	415	0.79	10
	Birch	323	1.29	428	0.85	10
	Oak	325	1.29	450	0.44	10
Safi et al. (2004)	Pine needles	290	0.71	390	–	15
		310	0.845	370	–	30

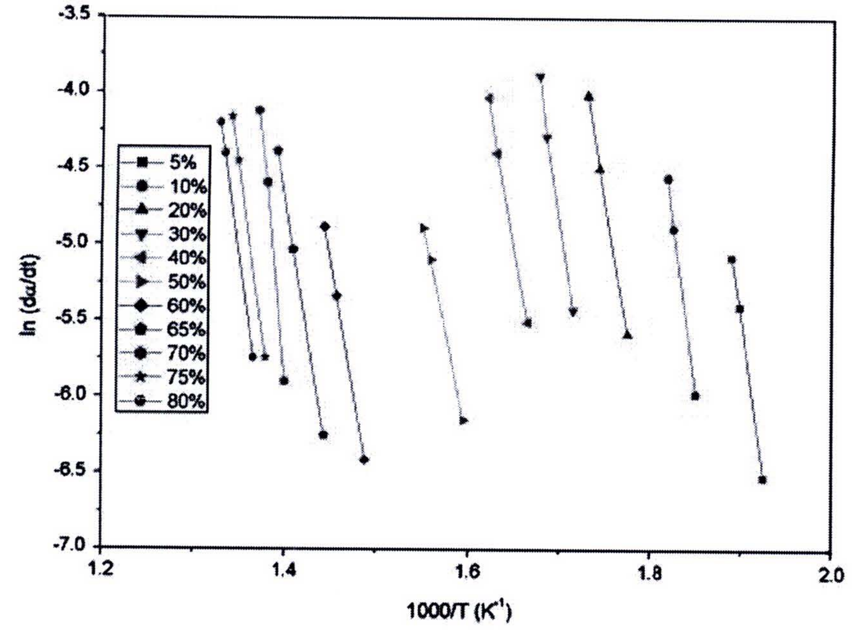

Fig. 3. Relationships between the rate of conversion with temperature for conversions of 5–80%.

Table 3
Calculated combustion kinetic parameters for Mimosa at each conversion.

References	Biomass		n	Conversion (%)									
				5	10	20	30	40	50	60	70	80	85
This work	Mimosa	E (kJ/mol)		344.24	366.98	285.95	319.27	268.80	235.23	284.21	497.53	341.54	399.34
		A (s^{-1})	0th	6.09×10^{31}	7.47×10^{32}	1.23×10^{24}	1.79×10^{26}	9.79×10^{20}	8.55×10^{16}	1.99×10^{19}	6.76×10^{33}	7.42×10^{21}	2.70×10^{25}
			1st	1.22×10^{31}	7.47×10^{31}	6.13×10^{22}	5.98×10^{24}	2.45×10^{19}	1.71×10^{15}	3.32×10^{17}	9.66×10^{31}	9.27×10^{19}	3.18×10^{23}
			2nd	2.44×10^{30}	7.47×10^{30}	3.06×10^{21}	1.99×10^{23}	6.12×10^{17}	3.42×10^{13}	5.54×10^{15}	1.38×10^{30}	1.16×10^{18}	3.47×10^{21}

tion and char combustion. The findings obtained here may be due to the fact that different lignocellulosic materials contain a varying degree of cellulose, hemicellulose, and lignin. It is widely accepted that thermal decomposition behaviour of biomass is affected by its chemical composition. Several studies reported that hemicellulose started to degrade first, followed by cellulose, and lignin (Gronli et al., 2002; Orfao et al., 1999). The higher degradation temperatures observed for Mimosa can be explained by its relatively high lignin content (33.9%).

Fig. 3 shows the relationship between $\ln(d\alpha/dt)$ and $1/T$ at various conversions from 5% to 80%. Thus, a family of parallel straight lines with a slope of $-E/R$ is obtained. From the slope of $\ln(d\alpha/dt)$ against $1/T$ at the conversion of 10%, the activation energy and the intercept ($\ln(A\alpha^n)$) can be obtained at each conversion. The variation of activation energy and the calculated pre-exponential factors assuming the reaction order as zeroth, first or second as a function of the conversion level, calculated using Eq. (5) is presented in Table 3. The activation energy for the thermal degradation of Mimosa in air atmosphere ranged from 235 to 498 kJ/mol, with an average value of 334 kJ/mol. Main decomposition appeared to occur at the conversions of 5–10% and 70%, where the activation energies were high and the pre-exponential factors were in the range of 10^{30}–10^{33} s^{-1}. At other conversions, the pre-exponential factors were found to drop rapidly to 10^{13}–10^{26} s^{-1}. The increase in activation energy at higher conversion may be attributed to ignition and oxidation of char residues. Fernandes et al. (2006) showed that during thermal decomposition of overlapping regions between cellulose and hemicellulose, and between hemicellulose and lignin, the associated activation energies were observed to jump radically. Similar observation was evident here, but at smaller rise. It was generally accepted that thermal decomposition was favoured in oxygen-containing atmosphere. A change from inert to oxidative atmosphere should result in an increase in apparent activation energy. The values found here were as much as 35 kJ/mol higher than those obtained from the pyrolysis of Mimosa reported in Wongsiriamnuay and Tippayawong (2010), at conversion up to 30%. But at higher conversions, the difference appeared to diminish. The observed fluctuation of activation energy at high conversions, around region for thermal decomposition of lignin in air, was similar to that reported by Fernandes et al. (2006). Table 4 compares the average activation energy among various biomass materials, obtained at similar temperature range. The average activation energy values for Mimosa was higher than those obtained from woods (Shen et al., 2009), and much higher than those from rapeseed, agro-residues and biowastes (Haykiri-Acma and Yaman, 2008; Kumar et al., 2008; Munir et al., 2009; Sun et al., 2010; Safi et al., 2004; Otero et al., 2010). Shen et al. (2009) reported the activation energies for wood species to be 145–210 kJ/mol while Munir et al. (2009), Kumar et al. (2008) and Sun et al. (2010) reported the range of 57–139 kJ/mol for agro-residues. Corn stalk was reported to have similar magnitude of kinetic parameters (Tian and Fu, 2009) to Mimosa. Its activation energy for thermal degradation in air atmosphere was reported to be about 350 kJ/mol. It was not yet known why Mimosa exhibited high activation energy. It was suggested that combustion rate could not only depend on the composition but also on the mutual interaction between the individual components (Rhen et al., 2007). Attempt was therefore made to relate these unique kinetic parameters with their chemical composition, shown in Tables 1 and 5. It was apparent that the chemical composition in terms of CHNO between these biomass materials and Mimosa were similar. It did not appear to have any significant correlation. With respect to the lignocellulosic composition, Mimosa was found to have higher lignin content and lower holocellulose, sum of hemicellulose and cellulose, content than other agro-residues. However, based on thermal decomposition of lignin, the activation energy obtained was small, compared to other components.

Table 4
Comparison of average combustion kinetic parameters between Mimosa and other biomass materials.

Reference	Biomass	Atmosphere	Heating rate (°C/min)	Temperature range (°C)	E (kJ/mol)
This work	Mimosa	Air	10, 30, 50	200–500	334
Haykiri-Acma and Yaman (2008)	Rapeseed	Air	20	127–752	21
Kumar et al. (2008)	Corn stover	Air	10	250–560	57
			30	250–560	126
			50	250–560	139
Munir et al. (2009)	Cotton stalk	Air	20	200–500	113
	Bagasse				75
	Shea meal				108
Shen et al. (2009)	Pine	Air	10	200–370	119
	Aspens				114
	Birch				116
	Oak				117
Shen et al. (2009)	Pine	Air	10	370–490	145
	Aspens				205
	Birch				210
	Oak				150
Sun et al. (2010)	Cotton stalk	Air	20	200–360	108
				360–500	125
Otero et al. (2010)	Sewage sludge	Air	5, 10, 25, 50	200–480	129
	Animal manure				133
Safi et al. (2004)	Pine needle	Air	10	192–503	85
			30	181–575	87

Table 5
Lignocellulosic composition and average activation energy between Mimosa and other biomass materials.

Reference	Biomass	Hemicellulose	Cellulose	Lignin	Atmosphere	E (kJ/mol)
This work	Mimosa	58.2 as holocellulose		33.9	Air	334
Tian and Fu (2009)	Corn stalk	16.8–35.0	35.0–39.6	7.0–18.4	Air	302.6
Barneto et al. (2010)	Hemicellulose	100			N_2	88.4
	Cellulose		100		N_2	203
	Lignin			100	N_2	75.1
Varhegyi and Antal (1989)	Hemicellulose	100			N_2	187
	Cellulose		100		N_2	213–234
Shen et al. (2009)	Pine	15.37	52.10	27.45	Air	119
	Aspens	19.06	60.70	14.80	Air	114
	Birch	24.79	56.47	12.17	Air	116
	Oak	28.97	53.95	9.43	Air	117

Furthermore, reported contents of lignocellulosic composition of these biomass materials showed variation (Garrote et al., 1999). Relation between chemical composition and activation energy was not conclusive. Other possible explanation may be associated with the presence and absence of mineral content in various biomass materials (Varhegyi and Antal, 1989). The resulting kinetic parameters were dependent on whether reaction mechanism of lignocellulosic decomposition was catalyzed or uncatalyzed. Biomass materials obtained from agriculture may have high mineral content from fertilization, compared to weeds like Mimosa. The effects of mineral content in biomass ash may be investigated further.

4. Conclusion

Thermal degradation of Mimosa under air environment was investigated using TGA at different heating rates. Kinetic parameters in terms of apparent activation energy and pre-exponential factor were determined. Oxidative thermal degradation of Mimosa exhibited two major mass loss stages due to devolatilsation and combustion. DTG curves showed similar peak decomposition temperatures to woods, but at higher temperatures than energy plants, agro-residues and biowatse samples. Increasing heating rate resulted in increasing mass loss rates, but delayed thermal decomposition to higher temperatures. During combustion, the kinetic parameters changed with conversion between 5% and 80%. The average activation energy was about 334 kJ/mol.

Acknowledgements

This research is supported by the Thailand Research Fund (contract no. RSA5080010) and Faculty of Engineering, Chiang Mai University. The Royal Golden Jubilee PhD scholarship (PHD/0047/2550) awarded to T.W. is greatly appreciated. Support from the Energy Research and Development Institute, Chiang Mai University is also acknowledged.

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INTERNATIONAL JOURNAL OF CHEMICAL
REACTOR ENGINEERING

Volume 8 2010 *Article* A50

Investigation of Light Tar Cracking in a Gliding Arc Plasma System

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ISSN 1542-6580

Investigation of Light Tar Cracking in a Gliding Arc Plasma System*

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Abstract

Utilization of biomass gasification technology is not widely adopted due largely to tars contained in the product gas that pose serious problems, especially in engine use. In this paper, a laboratory scale plasma system for light tar cracking was developed. The system was based on non-equilibrium plasmas generated from two gliding arc plasma in series. Light tar components were represented by naphthalene in nitrogen flow, generated at constant rates between 130 – 690 mg/m^3. Destruction efficiency and specific energy use were evaluated. It was found that destruction efficiency in the range of 70 – 95% could be achieved with a simple, single stage reactor. Plasma assisted tar decomposition was found to increase with applied electrical energy. Complete destruction (>99%) of light tars was obtained with the two-stage, gliding arc plasma system with applied electrical energy of about 1.8 – 2.9 kWh/m^3.

KEYWORDS: biomass, electrical discharge, gasification, gliding arc, plasma, tar decomposition

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*This work was supported by the Thailand Research Fund (contract no. RSA5080010) and Faculty of Engineering, Chiang Mai University. The authors are affiliated with the Department of Mechanical, Engineering, Chiang Mai University, Thailand.

1. INTRODUCTION

Biomass is one of the most important energy sources for the future. Gasification is the main conversion route for biomass energy utilization that generates a gaseous fuel. The producer gas can be used in internal combustion engines. However, deployment of this process is usually limited by the fuel gas quality where specially a high concentration of tars can cause operational problems such as blocking of gas cooler, filter elements and engine suction channels. Tar is a complex mixture of condensable hydrocarbons. It is defined as all organic contaminants with a molecular weight larger than benzene (Li and Suzuki, 2009; Maniatis and Beenackers, 2000). Control and conversion of tar is a key issue for successful applications of biomass derived producer gas. Tar removal methods may be categorized into two types depending on the location where tar is removed; in the gasifier, or after the gasifier (Devi *et al.*, 2003). Treatment of tar after the gasifier is normally adopted and can be done by two approaches; (i) physical removal, such as use of cyclone, filters, electrostatic precipitators and scrubbers, (ii) chemical removal, where the structure of tars is destroyed thermally and catalytically (El-Rub *et al.*, 2004; Han and Kim, 2008). Tar cracking by plasma is also possible.

Plasma technology can offer as alternative solution for thermal and catalytic treatment (Czernichowski, 1994; Chang, 2001). This process is capable of very high destruction efficiency, similar to incineration. Plasmas contain highly reactive species, such as electrons, ions and radicals which can enhance chemical reactions. Generally, plasmas can be divided into two categories: thermal plasmas and non-thermal plasmas. Non-thermal plasmas are low pressure plasmas characterized by high electron temperatures, and low ion and neutral temperatures. Thermal plasmas and non-thermal plasmas have been a subject of active research for many years, with the number of applications steadily growing. Investigations on reforming and destruction of organic compounds are increasingly being investigated (Yamamoto and Futamura, 1998; Kogelschatz, 2004; Paulmier and Fulcheri, 2005; Petitpas *et al.*, 2007). For these two general types of plasma discharges, it is impossible to simultaneously keep a high level of non-equilibrium, high electron temperature and high electron density, while most plasma chemical applications use high power and a high degree of non-equilibrium to support selective chemical processes. However, theses parameters can be achievable in gliding arc discharge. Gliding arc plasma has a complicated space-time structure including quasi-equilibrium and non-equilibrium periods as well as a fast transition between them. The fast transition is due to a specific ionization instability which has a strong non-linear behavior (Fridman *et al.*, 1994; 1999). It may be simply characterized by the presence of burning flames between two metal electrodes. This gliding arc plasma is not complex, can be generated at atmospheric pressure, and is able to produce energetic radical species, more active than non-thermal plasmas (Fridman *et al.*, 1999; Lin *et al.*, 2006; Indarto *et al.*, 2007). It offers high energy efficiency and selectivity for chemical reactions. The excitation energy can be delivered to specific molecules in the reacting gas mixture (Kim, 2004). The gliding arc plasma technology has successfully been used to decompose various organic compounds (Burlica *et al.*, 2008; Bo *et al.*, 2007, 2008; Indarto *et al.*, 2007). Pemen *et al.* (2002) reported the use of gliding arc discharge to remove tar downstream of a 1 kg/h biomass gasifier at varying temperatures. They found that tar conversion increased with applied energy, but with tar conversion of at most 40%. This technology appears to have great potential in removing tar from biomass gasification. However, there have been relatively few works with regards to plasma cracking of tar.

In this study, application of non-equilibrium plasma to cracking of light tar was investigated. A laboratory scale, gliding arc plasma system was designed and constructed. Naphthalene in nitrogen flow was simulated as a light tar. Preliminary experiments to determine tar destruction efficiency were conducted for a range of light tar concentrations and applied power input.

2. EXPERIMENTAL

2.1 Setup

Experiments were carried out using a laboratory scale gliding arc discharge reactor setup at atmospheric pressure. The gliding arc plasma reactor was a rectangular vessel with two divergent electrodes inside, shown in Fig. 1. The transparent, box-shaped vessel with a volume of approximately 15 cm^3 was made from acrylic panels with thickness of 5 mm, allowing visible observation of the discharge. The two knife-shaped electrodes were made of stainless steel with thickness of 3 mm. The length of the electrodes was 60 mm. The electrode gap at the entrance was fixed at 5 mm. Two sets of electrodes enable working with two gliding arc plasma reactors in series. The experimental set-up consists of a single gliding arc plasma reactor, or two reactors connected in series, a light tar generator, a power source, and a chemical and electrical diagnostic system (shown schematically in Fig. 2).

Each power supply was coupled to an AC neon transformer (LEIP EX 230A 15N) which was connected to 220V/50Hz. The resistances were used to control the current in the power supply and keep a non-thermal state in the gliding discharge. The maximum voltage and current were 15 kV and 30 mA (non breakdown), respectively. Electrical characterization of the power supply was performed using an oscilloscope. Tar is a complex mixture of condensable hydrocarbons, including single ring to five-ring aromatic compounds along with

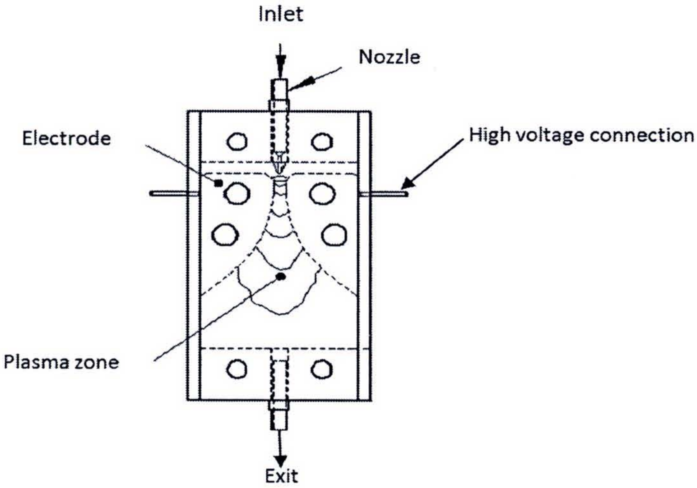


Figure 1. Configuration of the gliding arc plasma reactor

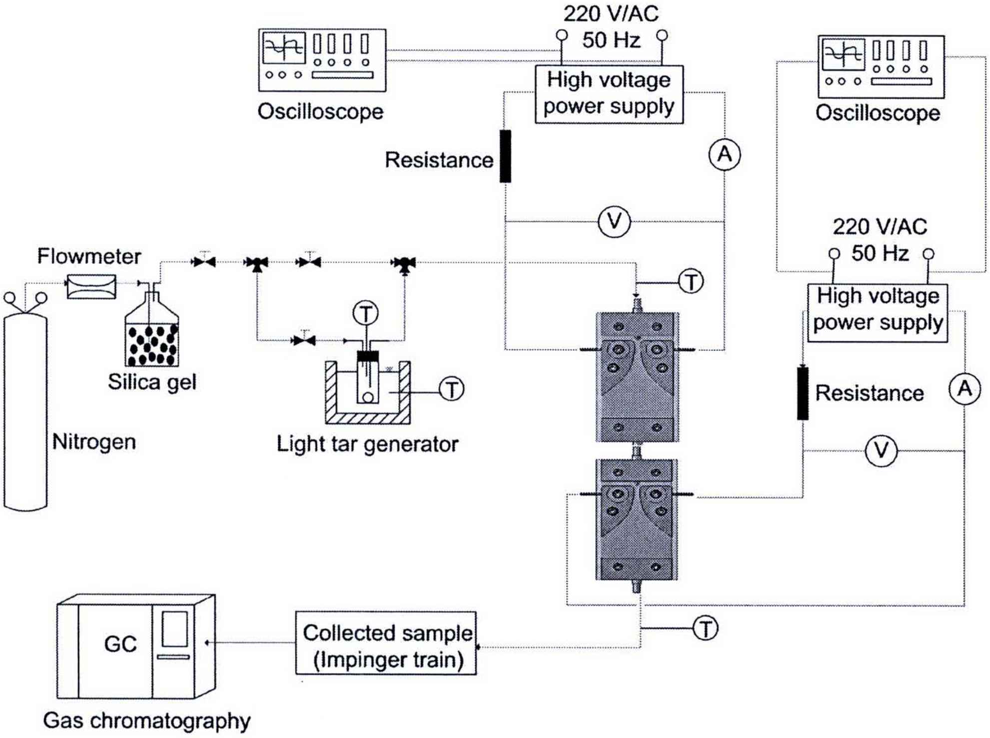


Figure 2. Experiment setup

other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PAH). Light tar consists mainly of light PAH compounds which condense at low temperature even at very low concentration such as indene, naphthalene, phenanthrene. In this work, naphthalene (Fig. 3) was used as a representative for light tar components (Nair *et al.*, 2003; Devi *et al.*, 2005). N_2 from a compressed tank was used as a carrier gas for naphthalene. The solid naphthalene was contained in a chamber immersed inside a temperature controlled water bath. Light tar was generated and maintained at a steady rate by means of a constant flow rate and constant bath temperature. The flow of nitrogen gas was controlled by a Dwyer flow meter model VFB-67-BV. Volumetric flow rate of medium gas can be varied between 5 to 15 lpm.

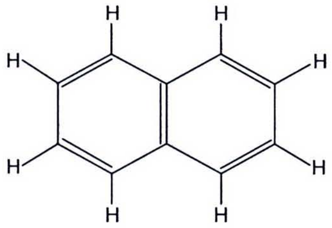


Figure 3. Naphthalene as a representative light tar component

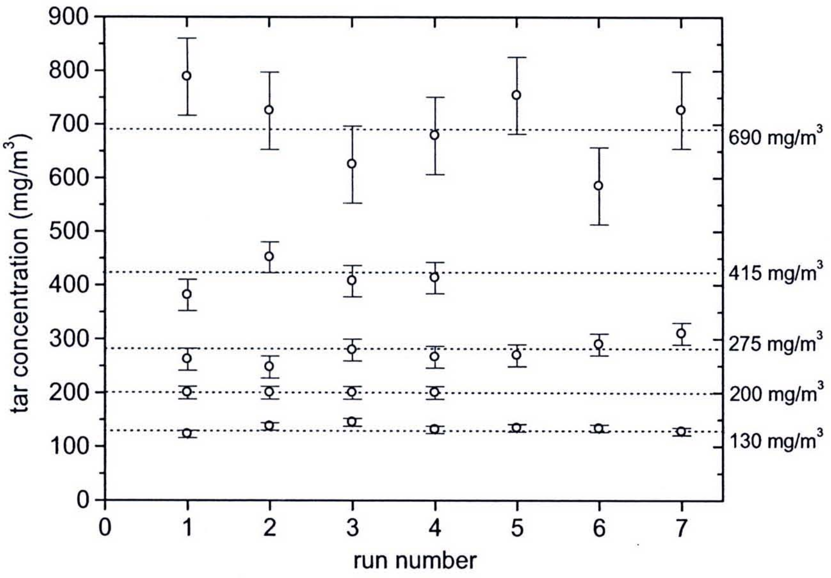


Figure 4. Repeatability pattern of tar generation

Fig. 4 shows repeatability characteristics of light tar concentrations generated. Inlet concentrations were able to adjust to 130, 200, 275, 415 and 690 mg/m^3. Error bars showed magnitude of standard deviation. Maximum variation was found to be within 10% of the mean concentrations considered.

2.2 Procedure

Initially, the water bath was switched on until the water temperature became steady. Pre-weighed naphthalene was then loaded into the tar chamber, and the gas valve opened to operate the tar generator. The tar containing gas was fed to the plasma reactor via heated tubing to prevent re-condensation. Voltage applied to the two electrodes was about 6.9 kV while input power was controlled at 125, 350, 550, 800, 1100 and 2650 W. The applied voltage and current were constantly monitored. The exit gas was passed through an impinger train via a heated tubing to collect tar in the gas stream. One experimental run was about 15 – 20 min. For each condition, repeated tests of between 3 – 7 runs were carried out. The concentrations of tar with and without plasma process were determined by gas chromatography – flame ionization analysis (Agilent GC-FID analyzer model 6890A G1540A, APEX ProSep PSI, HP5973 MSD system, HP-5 column) of samples collected by iso-propanol solvent in the impinger train. The instrument detection limit for naphthalene was 1.1 µg/L. Limited test on downstream gas composition was carried out using gas chromatography – thermal conductivity detection (Shimazu GC-TCD analyzer model GC8A, Restek ShinCarbon ST micropacked GC column). High velocity gas was injected between the electrodes through a nozzle with inner diameter of 1.5 mm.

Tar destruction efficiency and specific energy consumption were calculated from:

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \tag{1}$$

$$E = \frac{P}{Q_{gas}} \tag{2}$$

3. RESULTS AND DISCUSSION

3.1 General operation

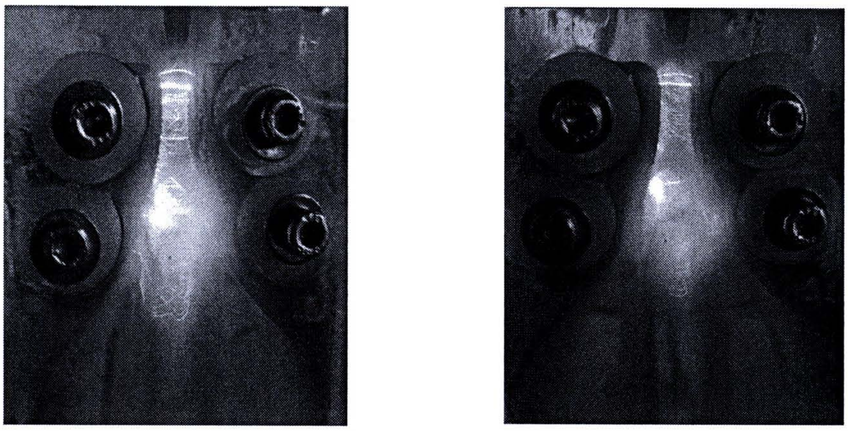
With regards to operation of the plasma system, a general trend similar to that reported by Paulmier and Fulcheri (2005) was observed. It was clear that successful ignition could be established instantaneously with stable plasma flame up to 15 lpm of gas flow. At higher flow rates, plasma flame became difficult to visualize. There was no electrical interaction and disturbance observed between the two gliding arc reactors. Continuous operation for several hours was carried out smoothly without any damages to the reactor system. Within the conditions considered, the degree of electrode erosion was found to be low.

3.2 Physical characteristics

Fig. 5 shows an example of the gliding arc plasma reactor in operation with N_2 flow through the gap. From simple visual observation, a plasma shower showed bright light of pinkish violet color with a number of visible sparks bridging between the two electrodes, covering almost the whole length of the reactor. This was the expected character of high ionized plasma density in N_2 discharge. The plasma flame appeared to stay constant in overall volume. Downstream measurements of temperature showed an increase from 100 to 150°C, which was negligible for effect of thermal cracking. When the naphthalene in N_2 flow was fed to the reactor, the plasma shower in the 1st reactor did not show any significant change in physical appearances. However, the color change of plasma to violet was observed in the 2nd reactor. This may be attributable to the presence of C_1-C_3 radicals resulting from decomposition of C_{10} in the 1st reactor. CN radical emission resulting from reaction of carbon and atomic nitrogen (Dinescu *et al.*, 1998) may also contribute to the observed color. However, it was also noticed that there was a deposition of dark brown solid particles, accumulated downstream of the system after prolonged test run. These deposits may be soot or high molecular weight compounds formed from decomposition reactions. The heavy compounds might be benzaldehyde, benzyl alcohol, ethylbenzene, styrene, and bibenzyl, as suggested by Grossmannova *et al.* (2007) for plasma conversion of toluene in inert atmosphere. Tar decomposition under non-oxidizing atmosphere may occur due to;

Cracking: $pC_nH_x \rightarrow qC_mH_y + rH_2$

Carbon formation: $C_nH_x \rightarrow nC + (x/2)H_2$



1st reactor 2nd reactor

Figure 5. Gliding arc plasma in action

Under partially oxidizing environment, the main reaction pathway of naphthalene decomposition by plasma was via oxidation, with intermediate byproducts such as naphthalene-dione and phthalic-anhydride (Nair *et al.*, 2004). Analysis of product gas samples downstream of the plasma reactor system revealed the trace amount of CO and no H_2, CH_4 and CO_2 were observed within the detection limit of the GC-TCD used. However, the source of oxygen causing CO production is not currently known.

3.3 Cracking efficiency and energy requirement

The light tar was injected to the plasma reactor at mean concentrations between 130 – 690 mg/m^3 and total flow rates of 5 – 15 lpm. Fig. 6 shows typical experimental results for decomposition of the light tar by gliding arc plasma at a fixed flow rate. For a single pass plasma reactor treatment of tar concentrations below 275 mg/m^3, it was found that destruction rates of more than 80% were achieved with the supplied power of about 350 W. At higher power (550 W), destruction efficiencies of 90 – 95% were obtained. At higher concentration of 690 mg/m^3, the decomposition rates were slightly less. It was apparent that the destruction efficiency increased with an increase in power input. However, higher powers were needed to establish plasma at higher flow rates of gas. It should be noted that chemical bond strength and molecular stability are the main factors that can determine the decomposition rate in the plasma process. Different types of compounds from different classes of tar would have different results (Indarto *et* *al.*, 2007; Bo *et al.*, 2008). Nonetheless, these results obtained here were very encouraging. The presence of plasma by arcs formation can enhance the ability to decompose the targeted compounds with high conversion efficiency. A number of experimental runs were subsequently conducted with the two-stage gliding arc plasma which was essentially two single-stage reactors in series. For all conditions considered, it was found that complete (>99%) destruction of light tar was obtained. Within the detectable limit of the GC-FID, there was no trace of tar collected downstream of the reactor system. The gliding arc plasma proved to be very promising as an alternative tool to decompose tar compounds from biomass gasification.

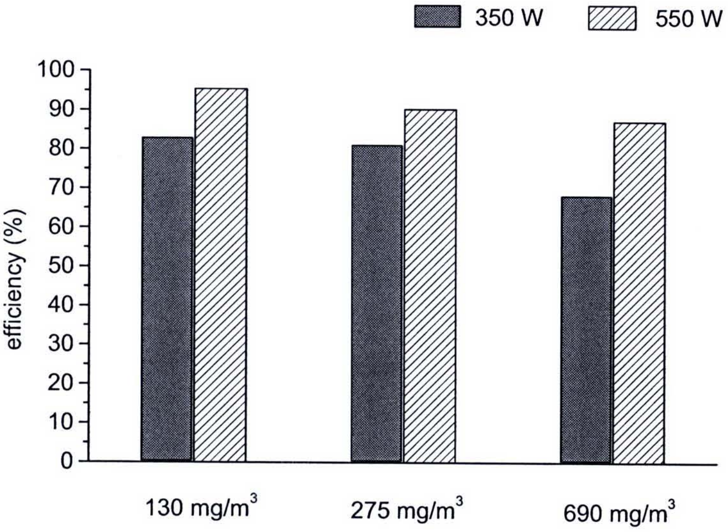


Figure 6. Variation in destruction efficiency of a single pass reactor with tar concentrations and applied powers

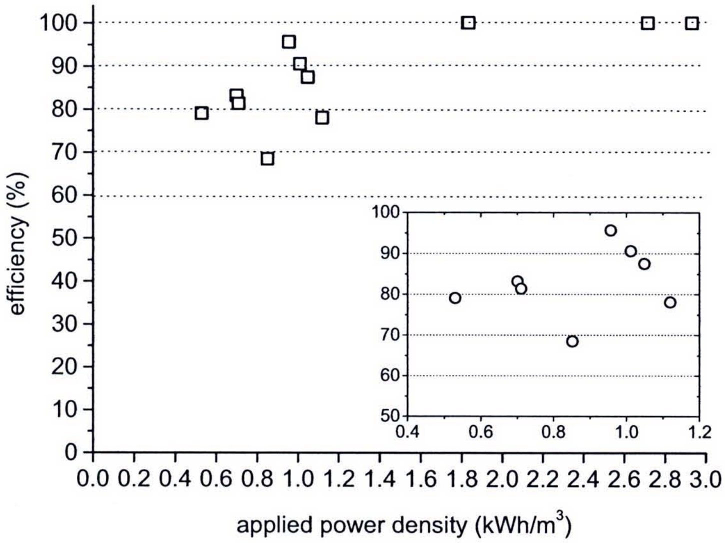


Figure 7. Overall performance of the plasma system at different power density

As far as energy utilization is concerned, maximum electrical power provided to the gas by the single-stage, and the two-stage plasma discharges were evaluated. Power input was in the range between 350 – 2650 W. Applied electrical energy to decompose light tar was estimated to be in the range between 0.5 – 2.9 kWh/m^3 (Fig. 7). This range can be divided into two groups; the single-stage system with <100% destruction and power density of 0.5 – 1.29 kWh/m^3, and the two-stage system with 100% destruction and power density of 1.8 – 2.9 kWh/m^3. For a given flow rate, it was clear that higher power density was required at higher concentration of tar. In some cases, higher flow rates resulted in slightly lower applied energy. Lower specific energy requirement means higher energy utilization efficiency. It seemed that high flow may promote transition from equilibrium to non-equilibrium state, hence, electrical energy was directly introduced to the reaction volume and utilized in decomposition process, rather than in heating the bulk gas. This observation was in line with that reported by Bo *et al.* (2007). Nonetheless, high energy consumption was a major drawback for plasma treatment. Techniques such as pulsed generation introduced in Burlica and Locke (2008) to reduce energy use should be adopted and investigated further.

Table 1 showed that the preliminary results of the plasma system developed here were comparable to other tar cracking techniques, with destruction efficiency around 90 – 100%. The main differences were in the operating temperatures which were much higher than the current system and carrier gas components which could interact with the light tar better than just pure N_2. For non-equilibrium plasma reactors, the present system appeared to demand higher energy requirement. It was clear that greater efforts remain to be performed in order to reduce input energy demand and test with real biomass tar that contains higher molecular weight components.

Table 1. Comparison between different light tar cracking techniques

	Houben *et al.* (2005)	El-Rub *et al.* (2004)	Nair *et al.* (2003)	This work
light tar model	naphthalene	naphthalene	naphthalene	naphthalene
concentration (mg/m^3)	2.6	4000	60 – 84	130 – 690
carrier gas composition	$N_2 + H_2 + CH_4$	$N_2 + CO_2 + H_2O$	$N_2 + CO_2$	N_2
type of cracker	thermal	catalytic	corona plasma	gliding arc plasma
working temperature (°C)	900 – 1150	900	400	100
gas flow rate (lpm)	-	1.2	4	5 – 15
destruction efficiency (%)	98 – 99	55 – 100	85 – 100	90 – 100
residence time (s)	1 – 12	0.3	-	0.1 – 0.3
power density (kWh/m^3)	-	-	0.08 – 0.14	0.95 – 2.9

4. CONCLUSIONS

In this work, a plasma reactor based on gliding arc was designed and constructed. The gliding arc plasma was successfully generated. The cracking of light tar in gliding arc plasma at atmospheric pressure was investigated. Significant destruction of tar was achieved at relatively low power input. With an increase in power input, tar decomposition rate increased. The observed rise in energy utilization efficiency may be attributed to the promotion of the equilibrium to non-equilibrium transition process. The single stage plasma reactor was reported to have up to 95% destruction efficiency. With the two-stage plasma reactor, complete destruction (>99%) of tar could be established. It was clear from these results that the gliding arc plasma has great potential to be applied as an alternative tool to destruct gaseous tar and other gaseous toxic compounds. However, it is noteworthy to recall that the presented results were based on naphthalene. In the next phase of research, application of this technology to real gasification product gas should be investigated.

NOTATION

C	mass concentration of naphthalene in N_2, mg/m^3
E	plasma energy density, kWh/m^3
n	number of mole or atom, -
P	applied power input, W
p	number of mole or atom, -
Q	gas flow rate, m^3/s
q	number of mole or atom, -
r	number of mole or atom, -
x	number of mole or atom, -

Greek Letters

η	destruction efficiency, %

Subscripts

gas	medium gas
in	inlet
out	outlet

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Renewable Energy from Thermal Gasification of a Giant Sensitive Plant (*Mimosa pigra* L.)

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Abstract: *A giant sensitive plant or Mimosa pigra L. is a fast growing weed that poses a major problem in agricultural areas. In this study, the stalks of Mimosa sample were collected, and air dried. They were subsequently milled, sieved and classified into fractions of uniform particle size. Proximate, ultimate and elemental analyses of the weed were performed. Composition and weight fractions of carbon, hydrogen, nitrogen, and oxygen were determined. Hollocellulose and lignin, the main constituents of biomass were also determined. Heating values of the weed was calculated, based on their composition and components, and compared with experimental results, following ASTM standards. Thermogravimetric analysis and gasification of Mimosa was carried out at atmospheric pressure in a laboratory-scale fixed-bed reactor to investigate mass loss rate, gas yields and product gas composition. Product gas was analyzed by gas chromatography for CO, CO_2, H_2, and CH_4. From the results obtained, Mimosa was found to be potentially suitable as biofuel. It contains high proportion of holocellulose, and is rich in carbon and volatile matter, and low in ash content. Its heating value, in comparison with other biomass, is higher than most agricultural residues. The product gas from gasification contains high CO and H_2, resulting in a useful lower heating value gaseous fuel. It was clear that the weed can be utilized as a useful renewable fuel source.*

Keywords: Biomass, Gasification, Mimosa, Renewable energy, Thermogravimetric analysis

1. INTRODUCTION

Biomass for energy application has gained increasing interests in Thailand, with a stiff competition with traditional food applications. Presently, interests in perennial rhizomatous grasses such as miscanthus (*Miscanthus*), switchgrass (*Panicum virgatum*), reed canary grass (*Phalaris arundinacea*) and giant reed (*Arundo donax*) as alternative biomass resources are growing because of their high yield potential, appropriate biomass characteristics, low input demand and positive environmental impact [1, 2]. Others include bamboo [3] and rapeseed straw [4]. Non-plantation biomass resources have been assessed for their energy potential in Thailand context and found to be promising [5]. In this investigation, weed such as a giant sensitive plant (*Mimosa pigra*) is viewed to have potential as a useful energy plant. So far, there have been relatively few literatures reporting on utilization of Mimosa as feedstock for bioenergy [6].

Energy may be recovered from biomass via various conversions [7, 8]. Choice of conversion process depends on the type and quantity of biomass feedstock, end use requirement, emission standards, economic conditions and project specific factors. In this work, attention has been paid to gasification since the process can yield a gaseous product that can be readily used in a burner or an internal combustion engine.

2. MATERIALS AND METHODS

2.1 Fuel composition analyses

Mimosa samples collected in agricultural zone in Chiang Mai, Thailand were used. The collected stalks were cleaned and air dried naturally in a dry store room at ambient condition. The dried samples were later ground in a high speed rotary mill, screen sieved and used for further analysis. Preparation of samples prior to analyses was conducted in accordance with TAPPI T 257 and T 264 standards. Contents of the major biopolymer constituents of the weed, holocellulose, lignin and solvent extractive components were evaluated using TAPPI standard methods. The solubilities of extractives in ethanol and benzene mixture as well as quantity of soluble substances in sodium hydroxide and in water were established. ASTM standard methods were followed to carry out proximate analysis for the samples. The carbon, hydrogen and nitrogen contents were determined using a CHN Elemental Analyzer. The oxygen content was calculated by difference. The heating value of the dried Mimosa stalk was determined in compliance with ASTM standard using a Parr bomb calorimeter. It is reported as a gross heat of combustion at constant volume.

2.2 Thermal gravimetry

The biomass materials were also analyzed by thermogravimetric analysis (TGA) method, using a TGA/SDTA 851e Thermogravimetric Analyzer. This high performance TGA analyzer has high sensitivity, vibration resistance and structure that permit rapid replacement of samples. Large number of samples can be analyzed in a short time and in succession. The system was logged to a personal computer for data handling and analysis. Prior to TGA, temperature, weight and sample platform calibrations were carried out. Each sample was placed in the platinum pan securely and in such a way that it was confined within the pan sides and not in contact with the sides of the oven. All handling of samples were done using brass tweezers to avoid contamination. The prepared samples were hanged down in the reaction tube in which the atmosphere can be controlled, and weighed by a sensitive microbalance with resolution of 0.1 µg. The sample was initially preheated to and equilibrated at 40°C in nitrogen under a flow rate of 90 mL/min for 10 minutes. The sample was then heated to 1200 °C at a constant heating rate of 30 °C/min. The purge gas can be switched to oxygen or air.

2.3 Gasification

Limited experimental runs on gasification of the biomass material were performed in a batch fixed bed gasifier setup, as shown in Figure 1. The samples were in size range of 3 – 6 mm. The reactor was cylindrical shaped with 0.5 m high and inside diameter of 40 mm. It was made of 5 mm thick stainless steel, surrounded on the outside by heating coil and thick insulating wool (Figure 2). The heating coil and the reactor were electrically separated by small ceramic spacers. There was a fixed grate between the middle and the bottom. The outlet of the gasifier is connected to gas coolers and traps where tarry components are removed, and to a sampling bag. Air is supplied from a compressed tank, serving as a purge gas and protective gas to avoid coking occurred on the surface of the reactor before and after operation and is measured with a calibrated flow meter. Reaction temperature is measured by a thermocouple inserted thru its cover and can be automatically controlled by means of a data logger. Prior to the test, the empty reactor was heated externally by an electrical heater for about 30 min. Pre-weighed batches of biomass materials were then introduced into the reactor. Air was supplied and regulated such that oxidation zone inside the gasifier can be established and gaseous products produced from the biomass is combustible. In this study, reactor temperature was obtained from thermocouple readings inside the reactor and represented as gasification temperature. The gaseous products were collected at the exit of the dry filter in a 0.10 dm^3 sampling bag. The volatiles were immediately sent for composition analysis. A Shimadzu Gas Chromatography model GC-8A was used to analyze CO, CO_2, H_2, CH_4, and N_2. The high purity standard gases were used to calibrate the instrument. The duration of operation for certain condition is determined by ensuring that no combustible gas is released and gas yield is dropped to more than 10% of its steady value. It should be noted that the residence time of the volatile phase is varied during the experimental run depending on the air flow rates. At the end of every experiment, the solid and liquid residues are weighed to determine mass balance. The gas yield is computed directly, based on its measured volume.

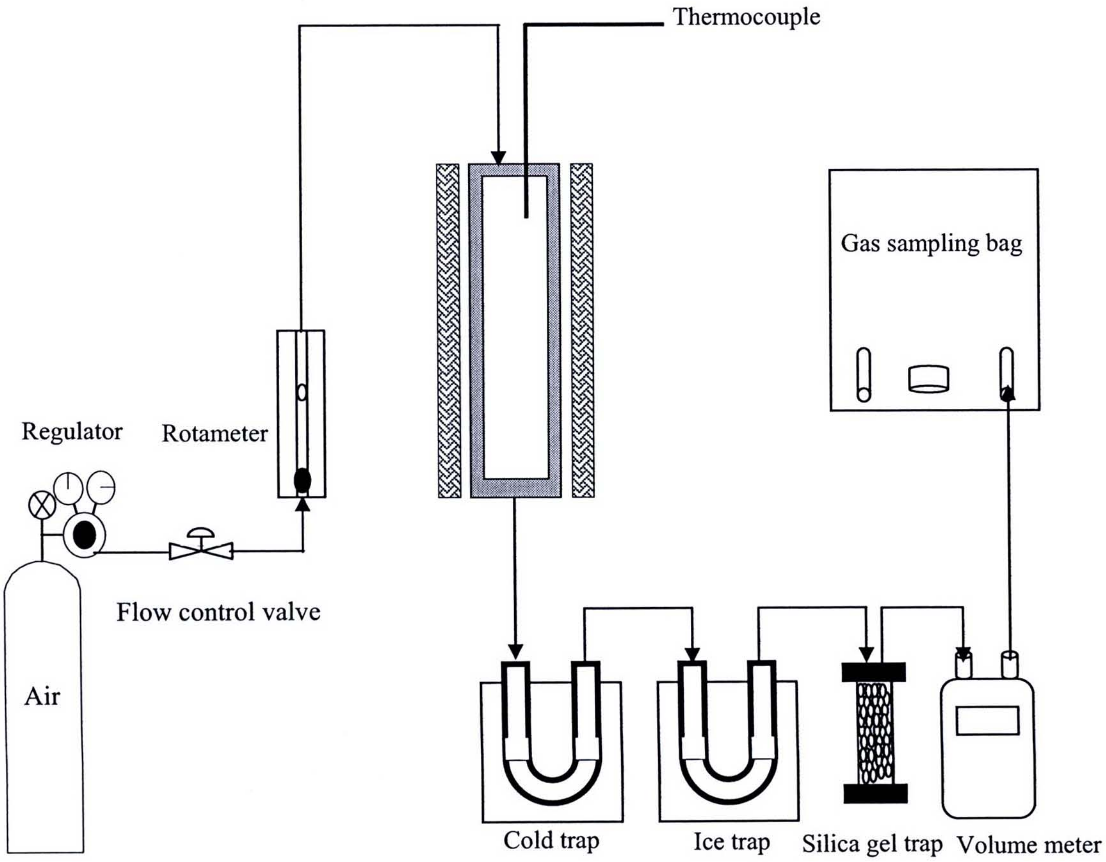

Figure 1 Gasification experimental setup

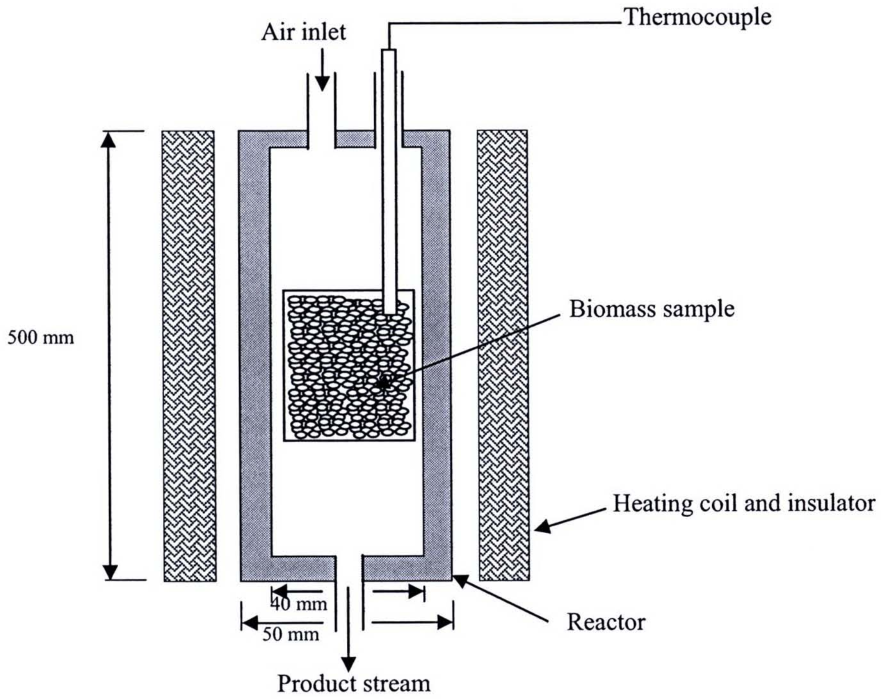

Figure 2 Configuration of the fixed bed gasifier

3. RESULTS AND DISCUSSION

3.1 Biomass composition

The heating value, proximate and ultimate analyses of the plant samples are listed in Table 1. Moisture content of the air dried samples ranged from 1.5 to 2.4% with average value of 1.6%. The ash contents of all Mimosa samples were 4.5% or less with an average ash content of 3.75%. This was quite low, and therefore the ash could be removed less frequently and continuously from a gasifier or combustor, without interfering with continuous thermo-chemical conversion. Compared to other major biomass feedstocks [9], this ash content is comparable to those found in woody biomass materials. Grasses and straws have higher ash contents. The volatile content was 71% and the remainder was fixed carbon at about 24%. High volatile matter in biomass generally increases tar content in the product gas and must be removed before it fed to an internal combustion engine. All samples showed similar gross heating values, averaging at 17.5 MJ/kg. This value is in similar magnitude to, but slightly lower than woody biomass and higher than most grasses and straws.

Table 1 Properties of the air dried Mimosa stalk

Property	Method	Quantity
Proximate analysis (% w/w)		
Moisture	ASTM D 3173	1.6
Volatile	ASTM D 3175	71.1
Fixed carbon	ASTM D 3172	23.6
Ash	ASTM D 3177	3.7
Ultimate analysis (%)	ASTM D 3174	
Carbon		43.9
Hydrogen		6.0
Nitrogen		1.4
Oxygen		48.7
H/C molar ratio	calculation	1.64
O/C molar ratio	calculation	0.83
Empirical formula	calculation	$CH_{1.64}O_{0.83}N_{0.03}$
Higher heating value (MJ/kg)	ASTM 5865	17.5

The carbon and hydrogen contents of the samples were at about 44%C and 6%H, respectively. The nitrogen content of the Mimosa samples was quite high, about 1.4%, when compared with other biomass feedstocks. But, this is considered to be low N content from combustion perspective. It would be beneficial in terms of minimal fuel bound N-to-NO_x conversion if the weed was used as fuel. Empirical formula of the weed, derived from the ultimate analysis, was obtained and can be represented as $CH_{1.64}O_{0.83}N_{0.03}$. It is interesting to note that there have been attempts to correlate proximate analysis results with elemental composition [10] and higher heating value [11] using results based on the proximate analysis of biomass materials. The correlations developed were applied to the Mimosa results. It was found to give the predicted heating value of 18.3 MJ/kg and predicted C and H contents of 47.7% and 5.6%, respectively, which were in agreement with experimental determinations. Their relative differences were within 7.5%.

Table 2 shows lignocellulosic characteristics of the plant. Holocellulose was found to be about 58%. Cellulose content in this range makes Mimosa a useful feedstock for conversion to fuels, chemicals, and other bio-based materials. The lignin level of 34% puts the weed at the high end of a range of 24-37% reported for softwoods and was greater than 11-27% found in non woody biomass [3]. Its high lignin content contributes to a relatively high heating value and structural rigidity, similar to softwoods. Meanwhile, the extractive substances were low. With regards to its solubility, it was observed that high proportion of the plant samples were soluble in dilute base solution. This was considerably higher than its solubilities in water, and ethanol-benzene mixture, respectively. Comparison of selected properties with other solid biofuels is presented in Table 3. The fuel characteristics of the weed appeared to be among the main solid fuels used.

Table 2 Lignocellulosic properties and solubility of the air dried Mimosa stalk

Property	Method	Quantity (% w/w)
Holocellulose	Wise method	58.2
Lignin	TAPPI T 222	33.9
Extractives, soluble in ethanol and benzene	TAPPI T 204	1.7
Solubility in hot water	TAPPI T 207	10.5
Solubility in cold water	TAPPI T 207	7.4
Solubility in 1% NaOH solution	TAPPI T 212	36.2
Solubility in ethanol and benzene	TAPPI T 204	5.2

Table 3 Comparison of selected characteristics between the air dried Mimosa and other solid fuels

Fuel property	Mimosa	Wood	Corncob	Rice husk	Lignite
Gross heating value (MJ/kg)	17.5	19.0	16.3	15.4	24.5
Moisture content (%)	1.62	1.5	10.0	8.2	4.5
Ash content (%)	3.75	2.5	3.4	13.2	7.2

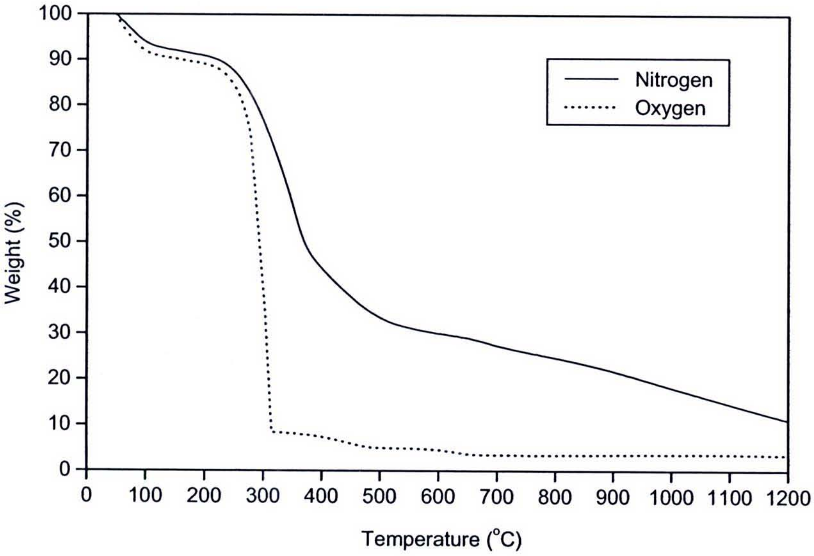

Figure 3 TGA thermogram for the air dried Mimosa sample

3.2 Thermal degradation characteristics

TGA was used to determine the thermal degradation of the biomass material. Figure 3 shows the TGA thermogram of weight change for Mimosa at heating rate of 30 K/min under N_2 and O_2 atmospheres. From the TGA data under N_2 environment, it can be seen that there was an initial weight loss of volatile component from the samples at approximately 250°C. The main devolatilization proceeded to about 600°C with total weight of 60%. Further thermal decomposition continued gradually at slower loss rate towards 1200°C. Under O_2 environment, similar thermal degradation character under N_2 environment was observed up to about 250°C. However, a major weight loss was evident between 280°C, and completed by about 300°C due primarily to oxidation. There was essentially no loss observed afterwards. The residual char and ash amounted to about 5%.

3.3 Gaseous fuel evolution

Preliminary results of the gasification experiments are shown in Table 4. For the given operating condition, the gas yield was found to be about 1.0 Nm^3/kg biomass. CO, CO_2 and H_2 were found to be 17.3%, 16.0% and 19.0%, respectively. This resulted in an average lower heating value of the producer gas of approximately 4.7 MJ/Nm^3.

Table 4 Results of the air dried Mimosa gasification

Property	Unit	Quantity
Test condition		
Equivalence ratio	(%)	0.25
Temperature	(°C)	900
Biomass feed	(g/hr)	10.0
Air flow rate	(dm^3/hr)	11.0
Average gas composition		
CO	(% v/v)	17.3
CO_2	(% v/v)	16.0
H_2	(% v/v)	19.0
CH_4	(% v/v)	3
O_2	(% v/v)	3.2
Nitrogen	(% v/v)	balance
Gas yield	(Nm^3/kg)	1.0
Lower heating value	(MJ/kg)	4.7
Cold gas efficiency	(%)	27
Carbon conversion	(%)	46
Product distribution		
Gas	% w/w	52
Liquid	% w/w	22
Solid	% w/w	26
Total	% w/w	100

4. CONCLUSIONS

Potential use of Mimosa as fuel was considered in this study. Physico-chemical characterization of the plant was conducted and gasification trials in a fixed bed reactor were investigated. It was found that Mimosa contains 59% holocellulose, 34% lignin and small amounts of extractive matter. It is rich in carbon and has considerable amount of volatile matter with relatively high heating value. It shares a number of desirable fuel characteristics with certain other biomass feedstocks. It appeared to present no obstacles in utilizing it as solid fuel with thermal conversion process. Present analyses indicated that Mimosa is potentially suited as useful solid biofuels and may be utilized through gasification at relatively moderate conditions. Its potential use as fuel is an important option for management of this weed. Further research may be required to develop cost effective management, harvesting and treatment prior to use in a power plant.

5. ACKNOWLEDGEMENTS

Supports from the Thailand Research Fund for this project and a Royal Golden Jubilee PhD scholarship awarded to TW are acknowledged. Chiang Mai University Graduate College is thanked for a grant awarded to PP.

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International Conference on Green and Sustainable Innovation 2009
December 2 – 4, 2009, Chiang Rai

Catalytic Destruction of Biomass Tar by Dolomite in a Dual Packed Bed Reactor

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Abstract

Biomass gasification contributes to bio-energy production without generating greenhouse gases into the environment. Commercialization of the technology is limited by tar contained in the product gas. Catalytic treatment of the gas can destroy the tar almost completely. In this study, a fixed bed catalytic reactor was designed, built and tested. A downdraft gasifier was used to generate a producer gas for tar cracking tests. This paper presents catalytic treatment of the producer gas in dual packed bed in a tar cracker using dolomite, calcined dolomite and char as catalysts. Experiments were carried out for a temperature range between 650 – 850°C. High tar conversions over 90% were obtained for all the catalysts used. It was evident that catalytic tar destruction in the dual catalyst bed could be a promising option for significant tar removal to be employed in a gasification system.

Keywords: Biomass gasification, Catalytic cracking, Dolomite, Tar removal

1. Introduction

With the depletion of fossil fuel sources as well as the global warming issues, utilization of biomass is getting increased attention as a potential source of renewable energy. Biomass fuels and residues can be converted to energy via thermal, biological and physical processes [1]. Biomass gasification is a complex thermochemical process including pyrolysis, partial oxidation of lignocellulosic materials. Product gas is composed of H_2, CO, CO_2, H_2O, CH_4 and various light hydrocarbons along with undesirable dust (ash and char), tar, NH_3, alkali (mostly potassium) and some other trace contaminants [2]. The continual build-up of condensable organic compounds (often referred to as tars) present in the product gas can cause blockages and corrosion, leading to a reduction in overall efficiency [3]. The producer gas can be used in engine and turbine for energy generation, fuel cells and methanol synthesis. Therefore, contaminants especially tars must be removed to meet the specific applications of the gas.

Commercial gasifiers use conventional filters and wet cleaning methods to remove the tar in the gas, discharging tar dissolved waste water that requires treatment before disposal. Thermal and catalytic treatment of the gas can ultimately destroy tar. Catalytic tar removal can operate at lower temperatures than thermal processes and result in high tar removal efficiency. Extensive reviews on the use of several catalysts for tar destruction can be found in the literatures [3-5]. Dolomite is usually employed due to its low cost. It is calcium magnesium ore with the general formula $CaMg(CO_3)_2$ that contains ~ 20% MgO, ~ 30% CaO, and ~ 45% CO_2 on a weight basis, with other minor mineral impurities. Calcination decomposes CO_2 to form CaO.MgO [5]. The use of dolomite inside gasifier and downstream reactor has been studied extensively. In this paper, investigation of the catalytic cracking of tar from biomass gasification in a dual packed bed reactor was presented.

2. Experimental Method

2.1 Equipments

Experimental setup includes a throat type, downdraft gasifier for producing the gas required for catalytic tar cracking tests. A laboratory scale catalytic tar cracker was built using stainless steel pipe with ID of 14mm and 70cm in length. It was heated by an insulated external electrical heating chamber, power rating of 3 kW. A dualpacked bed was housed inside the tar cracker. Internal temperatures along the cracker were measured by type K thermocouples. The outlet of the cracker was connected to a tar sampling impinger train. Gas flow rate was regulated by means of a pump and flow meters. The impinger train consists of six impinger bottles in which iso-propanol was used as solvent. The sketch of the experimental set up is shown in "Fig. 1".

2.2 Catalytic cracking

Catalytic cracking of biomass tar experiments were performed using dolomite, calcined dolomite and charcoal as catalysts. The particle sizes of the catalysts ranged from 2.12 mm to 4.75 mm, having average particle diameter of 3.41 mm. The bulk densities of the dolomite, calcined dolomite and charcoal were 1.23, 0.68, and 0.37 g/cm^3, respectively. Calcination of the dolomite was performed at 900°C for 2 hours in an oven. It was found that dolomite became softer after calcination, reducing its mechanical strength. The length of each catalyst bed inside the cracker was set at 270 mm.

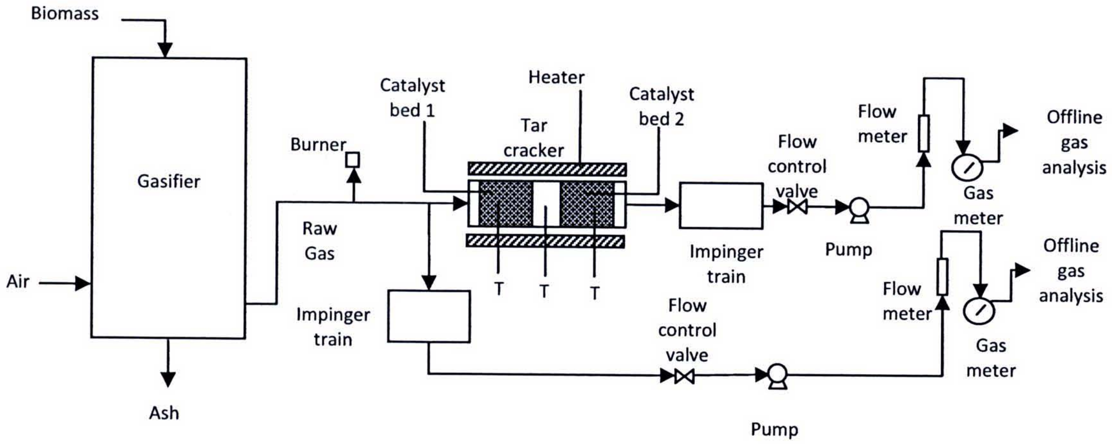


Fig.1 Experimental setup of a catalytic tar cracking system

2.3 Procedure

Cashew nut shells were used as biomass feedstock. Its moisture content was about 10.8% (as-received basis). The heating value and elemental composition of the cashew nut shells were taken from the works of Singh et al. [6], Das and Ganesh [7], shown in “Table 1”. At the start of each experiment, the gasifier was loaded with cashew nut shells and ignited at the bottom. The tar cracker was also simultaneously heated to reach the desired set point temperature, at a temperature range between 650 – 850°C. When the producer gas generated from the gasifier became combustible and operated in a stable manner, the cracking tests were started. The controlled parameters of the tar destruction test were temperature and residence time inside the dual packed bed. Each operation was performed for 15 – 20 minutes and repeated in triplicate for one controlled temperature. Tar containing gases upstream and downstream of the cracker were sampled separately. Measurement of tar content in the producer gas was carried out gravimetrically, following the method shown in tar sampling and analysis protocol [8]. Weight measurements for gravimetric evaporation were carried out using Metler digital analytical balance. Sample gases from the gasifier and the cracker after cleaning were collected in Tedlar gas bag and analysed offline by Shimadzu GC-8A/TCD using helium as carrier gas. Tar conversion, *X*, was calculated by;

$$X = \frac{c_{in} - c_{out}}{c_{in}} \times 100 \qquad (1)$$

where c_{in} and c_{out} are inlet and outlet tar concentrations (g/Nm^3), respectively.

Table 1 Properties of cashew nut shells

property	value
C	48.7 %
H	7.0 %
O	43.9 %
N	0.4 %
Heating value	17.6 MJ/kg

Table 2 Composition of the producer gas

component	%
CO	17.07
H_2	5.04
CH_4	3.15
CO_2	19.72
N_2	balance

3. Results and Discussion

3.1 Gasifier operation

The gasifier was able to start within 15 min and attain steady state operation from cold start in about 30-60 min. Although feeding was done intermittently, gasification seemed to operate well. Oxidation and reduction reactions appeared to proceed continuously. The system was able to run rather smoothly without any sign of significant deterioration. Fuel flow did not show any problem during the test runs. Nonetheless, poking at regular interval (1 h) was done to ensure trouble-free operation. Exit gas temperature of the gasifier was about 170°C. Producer gas was combustible, with bright orange flame. The composition of the gas was determined and shown in “Table 2”. The lower heating value of the producer gas was estimated to be about 3.51 MJ/m^3.

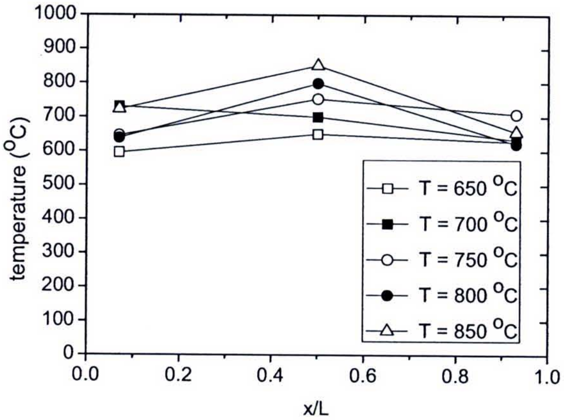


Fig. 2 Axial temperature distributions along the reactor length at different set point temperatures

3.2 Cracker operation

Prior to tar cracking tests, heater of the cracker was switched on to the set point temperatures. "Fig. 2" shows axial temperature profiles along the cracker length for each set point. At axial distance x = 0 represents the inlet and x = L is at the exit of the tar cracker.

3.3 Tar conversion

Temperature profiles inside the cracker are depicted in "Fig. 2". Tar conversion results are shown in "Fig. 3". These conversions were average values of triplicate experiments. Tar conversions with dolomite, calcined dolomite, and charcoal were found to be very high inside two catalyst beds reactor. The highest conversion obtained at 750 and 700°C for dolomite and calcined dolomite, respectively. Tar conversions above 90% were obtained with the charcoal as catalyst. The highest tar conversion of 99.5% was found at 800°C. "Fig. 4" shows tar concentration in the producer gas after treated with catalytic cracker. The final tar content was observed to be well below 35 mg/Nm^3 for all tested catalyst types and temperatures.

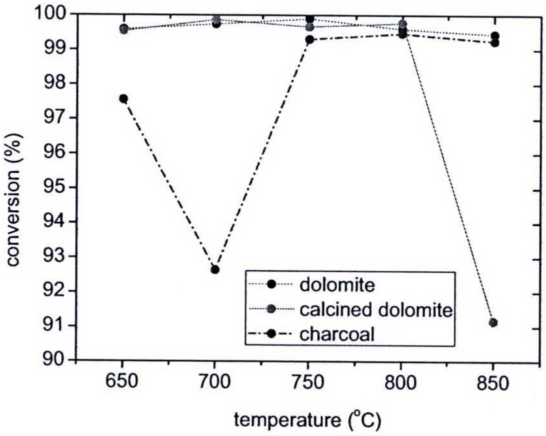


Fig. 3 Tar conversion for different catalysts

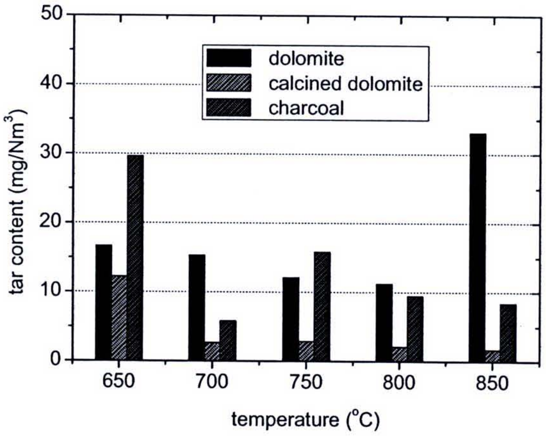
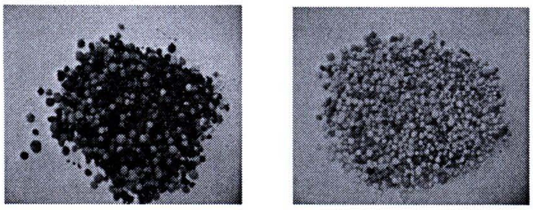


Fig. 4 Final tar contents in the treated producer gas after treatment with different catalysts

The observed fluctuation in conversion may be due to varying tar content in the producer gas with time and operating conditions. Reduction in tar conversion due to catalyst deactivation has not been observed for all the three catalysts. However, coke formation was observed with dolomite catalysts, as shown in "Fig. 5". It was found that the catalyst removed from first catalyst bed served as a guard bed and coke formation was severe. The second catalyst bed appeared to be less affected. Coke formation for calcined dolomite and charcoal was not clearly evident and difficult to identify.



(a) (b)

Fig. 5 Appearances of spent dolomite (a) first bed discharge and (b) second bed discharge

4. Conclusion

In this work, a catalytic tar cracker was designed and tested. Low cost catalysts were used. The use of dolomite, calcined dolomite and charcoal in a dual bed catalytic reactor showed over 90% tar reduction.

Catalytic hot gas conditioning of the producer gas to reduce the tar content doesn't produce waste water. Since the low cost and abundance the catalysts used in this study, it might be more economical than using expensive metal and noble synthesized catalysts. It can cut the excess equipment costs since the first bed serves as a guard for the second bed. Moreover, it could be combined with metal catalyst in second catalyst bed with the first guard bed so that high quality syngas could be generated.

5. Acknowledgement

Supports from the Energy Research and Development Institute, and the Graduate School, Chiang Mai University to ST, supports from the Thailand Research Fund (contract no. RSA5080010) and a Royal Golden Jubilee PhD scholarship awarded to TW are acknowledged.

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Gasification of Giant Sensitive Plants in a Fixed Bed Reactor

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Abstract: A giant sensitive plant (Mimosa pigra L.) is a fast growing and spreadable weed. It infests strongly along the rivers, surrounding large reservoirs, wetland reserves and agricultural fields. Its invasion threatens the production and preservation values of wetlands, and poses a major problem in agricultural areas. To avoid food-fuel dilemma, the weed may be utilized as a biorenewable energy source. In this study, it was used as feedstock for generation of producer gas. Mimosa sample were collected, and air dried. They were subsequently milled, sieved and classified into fractions of uniform particle size between 0.3 and 0.6 mm. Fuel characterization was performed using proximate and ultimate analyses. Gasification of giant sensitive plants was carried out at atmospheric pressure in a laboratory-scale fixed bed reactor to investigate the effect of reactor temperature and catalyst biomass ratio on gas yields and product gas composition. The product gas from thermochemical process was found to contain high CO and H2 which was a useful low heating value gaseous fuel. With an increase in temperature, gas yield was found to increase while char and tar were found to decrease. Increasing catalyst to biomass ratio was found to result in an increase in hydrogen, and a decrease in carbon monoxide. It appeared that the weed can be utilized as a useful renewable fuel.

Keywords: Biomass, Gasification, Mimosa, Renewable energy, Fixed bed.

1. Introduction

Mimosa, known in Thai as a giant sensitive plant, is a native plant of Central and South America. It was purposely introduced to Thailand in the late 1940s as a green manure and cover crop in tobacco plantations [1]. It is a leguminous thorny shrub that can grow to a height of six meters. Mimosa is able to form mono-specific stands, replacing the native wet vegetation and thereby reducing the available habitats of native flora and fauna. It is considered to be one of the worst environmental weeds of wetland in Thailand. When faced with an extensive weed infestation, it is natural to find ways to utilize it. Mimosa has been utilized for its ornamental value, medicinal use, green manure and erosion control. It has also been used as animal feed, timber and biomass material [1]. In Thailand, it has been used for firewood, temporary fences, and tested for fiberboard. However, the use is still limited in rather small scale applications. Alternative energy utilization method may offer different options and a mean for the weed management.

Thermochemical processing is recognized as the most important available technology for biomass conversion. Gasification is viewed to be a suitable conversion technology that offers high thermal efficiency and environmental acceptability. Gasification process is favourable for producing low to medium calorific value gas. If the weed is gasified efficiently, it may generate a high yield of clean product gas. Thermal decomposition of mimosa has been investigated [2, 3]. It was viewed to have potential as a bioenergy source via gasification. However, tar can potentially impair the product gas quality. Using of catalysts in the gasification process has been proved to be an effective method to reduce tar and improve gasification efficiency. Dolomite is among the cheapest and most available catalysts used to control tar. Natural dolomite has been shown to reduce tar content in producer gas [4, 5].

In this work, giant sensitive plants were used as a biomass feedstock for the generation of producer gas. A laboratory scale, fixed bed reactor was developed. The thermochemical conversion of mimosa was performed in the fixed bed reactor. The influence of different operation conditions, including reactor temperature and catalyst to biomass ratio on product yields (gas, char, and tar) and the composition of fuel gas in terms of H_2 and

H_2/CO was investigated. Air was used as gasification medium. Natural dolomite was used as an *in situ* catalytic gas conditioning agent.

2. Experimental setup

2.1. Sample characterization

Mimosa samples collected in agricultural zone in Chiang Mai, Thailand were used. The collected stalks were cleaned and air dried naturally in a dry store room at ambient condition. The dried samples were later ground in a high speed rotary mill, screen sieved and used for further analysis. The proximate analysis of the weed was carried out according to standard norms. The determination of moisture, volatile matter and ashes was performed following the standards; ASTM D 3173, ASTM D 3175. ASTM D 1372, ASTM 3177, respectively. The fixed carbon was calculated by difference to 100%. The determination of the ultimate analysis was made using a CHN-932 elemental analyzer (ASTM F 3174). The higher heating value of the weed waste was determined with a Parr calorimeter bomb (ASTM 5865). These parameters are displayed in Table 1. One can see that the weed has a high content of volatile matter and low content of ash, which is very interesting with respect to its applications in gasification and pyrolysis processes. The low N content ensures that thermal NO_x formation during the gasification process is negligible.

2.2. Test apparatus and procedures

Gasification experiments were performed at an atmospheric pressure using air as gasification medium. The experimental setup is shown schematically in Fig. 1. The fixed bed reactor was equipped with electric heaters around its perimeter which was covered with a thick insulation layer. Its setup consists of the fixed bed reactor, an air compressor and an feed air heater. The reactor was made of 1Cr18Ni9Ti stainless steel tube. The effective height of the reactor was 900 mm, with an internal diameter of 60 mm. Two type K thermocouples were used to measure and control the temperatures in the middle of the gasifier and the biomass in a basket.

Table 1. Properties of the air dried mimosa stalk.

Property	Quantity
Proximate analysis (% w/w)	
Moisture	1.6
Volatile	71.1
Fixed carbon	23.6
Ash	3.7
Ultimate analysis (% w/w)	
Carbon	43.9
Hydrogen	6.0
Nitrogen	1.4
Oxygen	48.7
Higher heating value (MJ/kg)	17.5

A collection module was used as cooling unit for fuel gas cooling and tar capture. It consists of two series of impinger bottles containing a solvent for tar absorption, placed separately in two cold baths. The first three impinger bottles were immersed in a temperature below 5 °C, whereas, the next three impinger bottles were cooled at a temperature under −20 °C which tar and moisture will be completely collected. The tar aerosols were collected by both condensation and absorption in the solvent. Each impinger bottle was filled with approximately 100 ml of isopropanol, which was considered to be the most suitable solvent for tar absorption [5]. The gas flow rate was measured with a volume meter. The cool, dry, clean gas was sampled using gas bags and analyzed on a Shimadzu Model GC-8A gas chromatograph fitted with a ShinCarbon ST Micropacked column and a thermal conductivity detector, for measuring volumetric concentration of H_2, O_2, N_2, CH_4, CO,

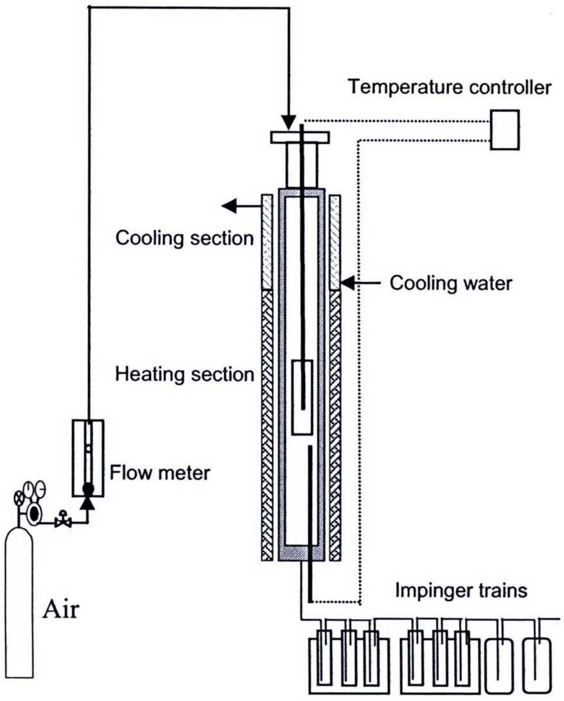

Fig. 1. Gasification experimental setup.

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CO_2. Standard gas mixtures were used for quantitative calibration.

Initially, the electric heater was switch on to heat the reactor. Once the set point temperature was achieved in the gasification reactor, the biomass was displaced from the cooling section to the heating section. Air was fed from the top of the gasification reactor. When stabilization was reached with respect to the temperatures, gas sampling and analysis were carried out. It was normally completed in about 20 min. Experiments were performed for (i) air gasification at 500 cm^3min^{-1} with varying temperature between 600 – 900°C and (ii) catalytic gasification with natural dolomite at varying proportions (% w/w referred to catalyst and biomass ratio) at 900°C with the same air flow condition. All experiments were carried out isothermally and initial mimosa mass of 10 g was used.

3. Results and discussion

3.1. Product yields

Fig. 2 shows effect of reaction temperature on the product yields from gasification of mimosa without presence of catalyst. The gas yields were found to increase from about 51% to 64% as the reaction temperature was raised from 600°C to 900°C. The char and tar fractions appeared to decrease with increasing temperature. Changes from 700°C to 800°C showed only marginal effect on the yields. Fig. 3 shows the product yields from gasification of mimosa at different catalyst to biomass ratios between 0.5 – 2.0 at a fixed temperature of 900°C. It was observed that while the char yield stayed relatively constant, the gas yield appeared to go through a maximum of 72% at a catalyst to biomass ratio of 1.0.

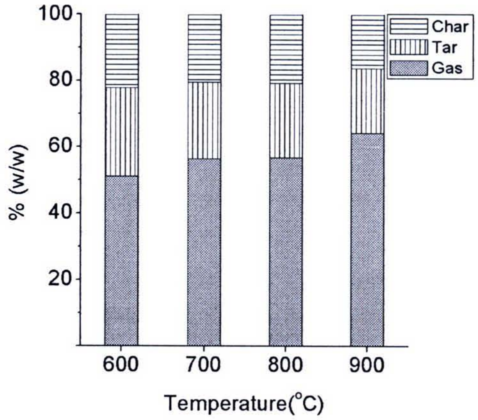

Fig. 2. Effect of reaction temperature on yields of gasification products

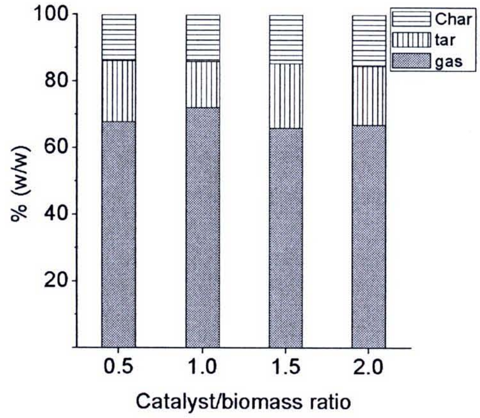

Fig. 3. Effect of catalyst/biomass ratio on yields of gasification products

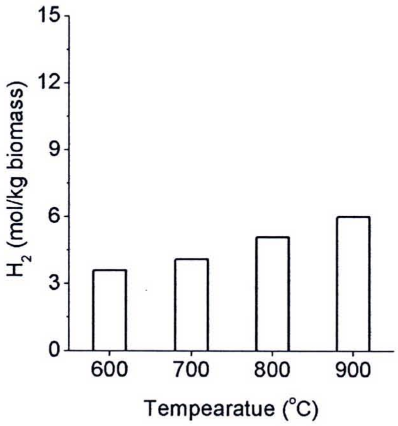

Fig. 4. Effect of reaction temperature on H2 yields.

3.2. H_2 and H_2/CO yields

Figs. 4 and 5 show effects of reaction temperature on the H_2 and H_2/CO yields from non-catalytic gasification. It can be seen from the experimental results that both the hydrogen yields and hydrogen to carbon monoxide ratios were primarily influenced by the operating temperature. Changing the temperature from 600 to 900°C resulted in an increase in the H_2 yields [6, 7], while H_2/CO yields were found to decrease slightly from 0.72 to below 0.60. The increases of the hydrogen fraction with

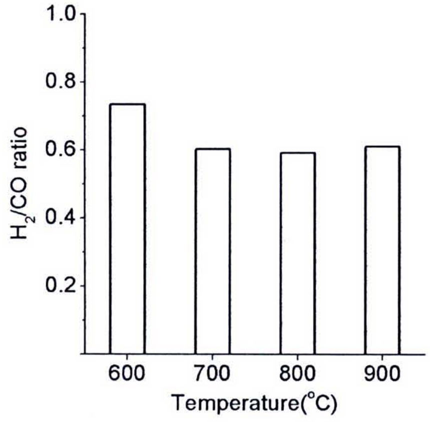

Fig. 5. Effect of reaction temperature on H_2/CO ratio.

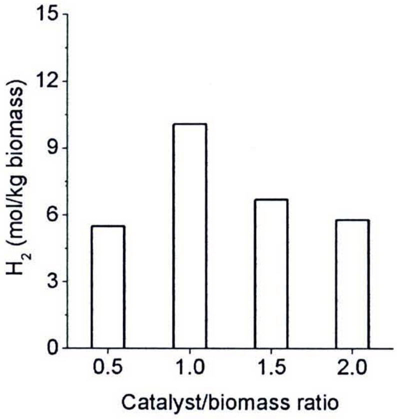

Fig. 6. Effect of catalyst/ biomass ratio on H_2 yields.

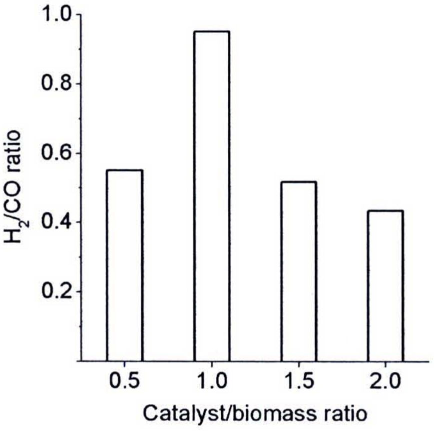

Fig. 7. Effect of catalyst/biomass ratio on H_2/CO ratio.

Table 2. Comparison of H2 yields for different types of biomass without catalyst.

Reference	Biomass	Temp (°C)	H2 yield (%)
This work	Mimosa	900	17
[6]	Sawdust	900	38
[9]	Saw dust	810	10
[9]	Wood	550	8
[10]	Rice straw	800	10
[10]	Rice straw	900	23

Table 3. Comparison of H_2 yields for different types of biomass with dolomite catalyst.

Reference	Biomass	Temp (°C)	H_2 yield (%)
This work	Mimosa	900	26
[10]	Rice straw	900	37
[11]	Sawdust	800	11
[12]	Pine sawdust	850	52
[13]	Pine sawdust	750	51

temperature were due to the greater production of gas in the initial pyrolysis (faster at higher temperatures), and the endothermic reactions of gasification of the char, which increases with temperature. It was clear that temperature has integrated effects on these results.

The effects of catalyst to biomass ratio on H_2 and H_2/CO yields when the reactor temperature was kept constant at 900°C are shown in Figs. 6 and 7. Generally, the H_2 yields were observed to increase with the presence of catalyst. The peak value of H_2 yield appeared at the catalyst to biomass ratio of 1.0 was twice as much as that at similar condition without the catalyst. This may be attributed to an increase in surface reaction area on the dolomite, greater the contact area between the biomass and the dolomite, leading to higher chemical reaction rates and gasification reactions [8]. However, increasing catalyst/biomass ratio did not prove to increase the hydrogen yield further. With respect to H_2/CO ratios, similar pattern to H_2 yields was observed that a maximum ratio of 0.95 was obtained at catalyst to biomass ratio of 1.0. However, at other catalyst to biomass ratios, the H_2/CO yields appeared to be slightly lower than the value at similar condition without the catalyst.

3.3. Comparison with literature

H_2 yields obtained from gasification of mimosa in this study were compared against those obtained from other types of biomass at similar thermal conditions. Results (in % by volume) are shown in Tables 2 and 3 for the cases with and without catalyst, respectively. It was found that H_2 yields were comparable to other biomass considered.

4. Conclusions

In this work, air gasification of giant sensitive plants under atmospheric pressure in a fixed bed reactor has been carried out with and without dolomite as a catalyst. Effects of reaction temperature and catalyst to biomass ratio have been investigated. Gas yields were found to increase with increasing temperatures. With catalysts, over 60% gas yields were obtained. Increase in temperature resulted in an increase in H_2 yields. The H_2 yields were found to increase further with presence of catalyst. A peak of H_2 yield was observed at catalyst to biomass ratio of 1.0. Producer gas yields and composition obtained from gasification of mimosa were in similar magnitude and comparable to other types of biomass. Mimosa appeared to have potential as a biofuel candidate.

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Acknowledgements: This research is financially supported by the Thailand Research Fund (no. RSA5080010) and Faculty of Engineering, Chiang Mai University. The Royal Golden Jubilee PhD scholarship (no. PHD/0047/2550) awarded to TW is greatly appreciated. Supports from the Energy Research and Development Institute, Chiang Mai University are also acknowledged.