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Energy Fuels, **2008**, 22 (1), 24-30 • DOI: 10.1021/ef7002848 • Publication Date (Web): 29 September 2007

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Pyrolysis of Rice Straw Using Radio-Frequency Plasma[†]

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Received May 28, 2007. Revised Manuscript Received August 21, 2007

In this study, a radio-frequency (RF) plasma thermolysis reactor was used for pyrolyzing the biomass waste of rice straw. The effects of some major system parameters on the performance of the pyrolysis of rice straw via RF plasma were studied and elucidated. Examining the characteristics of the RF plasma thermolysis reactor with the working gas nitrogen indicates that as the loading power (P_{WL}) increases from 137 to 591 W, the plateau temperature (T_P) of plasma increases from 607 to 954 K. The corresponding times of t_H to reach T_P (the corresponding t_H is denoted as t_{HP}) at 607 and 954 K are about 5 and 2 min, respectively. Thus, a higher P_{WL} gives a higher T_P with a shorter t_{HP} . The times of t_H with P_{WL} of 308, 363, and 591 W to reach a setting temperature (T_S) (the corresponding t_H is denoted as t_{HS}) at 783 K are about 5, 1.5, and 0.67 min, respectively. Again, a higher P_{WL} needs a shorter t_{HS} to reach the same T_S . No tar product is formed via pyrolysis using RF plasma, while about 1.5 wt % of tar is produced using traditional electric–thermal heating. Thus, the gaseous products obtained via the former method would contain more hydrocarbons (HCs) of low molecular weight than those via the latter method. This indicates that the ability of cracking HCs via the former is better than the latter, supporting the idea that the former can provide syngas with better quality.

Introduction

Bioenergy from biomass has the potential to provide a significant portion of the projected renewable energy provisions for the future. Among the available biomasses, rice straw is one of the favorable bioenergy sources because it is the residue from the end use of the biomass products. The reutilization of rice straw not only saves the cost of disposal but also produces valuable bioenergy, achieving the goal of resources recovery and reuse. Taiwan is located in the subtropics and has excellent farming technology, thus producing abundant biomasses. However, this also results in a significant amount of agriculture wastes to be treated, with the rice straw contributing the most. In Taiwan, rice is one of the principal foods. According to the statistics of in season agricultural products of Taiwan, the total cultivated area is 230 000 ha. The rice straw generated after being reaped from rice is about 6 tons ha⁻¹. Thus, the total annual generation of rice straw is about 1.4 million tons, including the first and second crops. Its common treatment is on-site burning for producing manure. However, the open burning is harmful to the air quality and environment. Among

the available biomasses, rice straw waste is one of the favorable bioenergy sources because it is the residue from the end use of the rice. The reutilization of rice straw waste not only saves the cost of disposal but also produces valuable bioenergy, achieving the goal of resources recovery and reuse.

Two main disadvantages of the pyrolysis and gasification of biomass wastes for producing medium calorific value gases via the traditional thermolysis technology are the following: (1) the gas yield is very low, reducing the energy value of gas, and (2) the amount of tar in the gas is high, causing corroding problems in the gas-collecting equipment.^{1–3} Adding catalyst in the pyrolysis or gasification of biomass is helpful for the product quality. Atutxa et al.⁴ pointed out that adding HZSM-5 catalyst can produce more gas products in the pyrolysis of sawdust. Waldner and Vogel⁵ found that joining Ni-catalyst in the gasification of sawdust can get higher yield in output syngas (0.33 g CH₄ per gram of wood). To increase the liquid yield, Gullu⁶ used Na₂CO₃ and K₂CO₃ as catalysts in the pyrolysis of hazelnut shell, tea waste, and yellow pine. The results indicated

[†] Presented at the International Conference on Bioenergy Outlook 2007, Singapore, April 26–27, 2007.

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(1) Caldeira, M. I. K.; Benford, G.; Criswell, D. R.; Green, C.; Herzog, H.; Jain, A. K.; Kheshgi, H. S.; Lackner, K. S.; Lewis, J. S.; Lightfoot, H. D.; Manheimer, W.; Mankins, J. C.; Muel, M. E.; Perkins, L. J.; Schlesinger, M. E.; Volk, T.; Wigley, T. M. L. *Science* **2002**, 298, 981–987.

(2) Bridgwater, A. V. *Chem. Eng. J.* **2003**, 91, 87–102.

(3) Chen, G.; Andries, J.; Luo, Z.; Spliethoff, H. *Energy Convers. Manage.* **2003**, 44, 1875–1884.

(4) Atutxa, A.; Aguado, R.; Gayubo, A. G.; Olazar, M.; Bilbao, J. *Energy Fuels* **2005**, 19, 765–774.

(5) Waldner, M. H.; Vogel, F. *Ind. Eng. Chem. Res.* **2005**, 44, 4543–4551.

(6) Gullu, D. *Energy Sources* **2003**, 25, 753–765.

that adding Na_2CO_3 is better than K_2CO_3 to give more liquid products. The humidity is also an enhancing factor. Adding steam can raise the liquid products in the pyrolysis of sawdust.⁷ The two disadvantages of the traditional thermolysis of biomass can be overcome by adding catalysts. However, the improvement of product quality for practical use is still not enough.

In order to overcome the disadvantages of thermolysis using traditional heating methods, a radio-frequency (RF) plasma heating method, which is also called the capacitive dielectric heating method, may be one of the alternative choices. The RF plasma heating method employs the alternating current with high frequency and voltage to build up an electromagnetic field producing plasma to induce the target material resulting in the vigorous colliding, rubbing, and, thus, self-heating. The RF plasma thermolysis reactor used in this study can be operated with changes of output voltage, pressure, energy density, and gas temperature. It can give better quality products under high frequency (10^5 – 10^7 Hz, e.g., at 13.56 MHz), high output power (as high as 2000 W), and low pressure (10^3 – 10^6 Pa). As the material is heated, pyrolysis occurs. The heating method using RF has many advantages such as a high heating rate (HR), short heating time (t_H), low heat loss, and low residual tar. The notations t_{HP} and t_{HS} denote the values of t_H to reach T_P and T_S (the setting temperature), respectively. Hence, this novel method can overcome the problems encountered in the traditional pyrolysis of biomass.^{2,3,8–10}

A low tar content in the product obtained from RF plasma thermolysis can be achieved because high energy species, such as electrons, ions, atoms, and free radicals, produced from RF plasma can enhance the decomposition of tar.¹¹ Tang and Huang¹¹ used RF plasma pyrolysis to treat the biomass of sawdust at various operating pressures (3000–8000 Pa) and input powers (1600–2000 W). On average, the gas yield can reach 66 wt % of the biomass feed at an input power of 1800 W and an operating pressure of 5000 Pa. The total content of CO and H_2 in the gas product reached 76 vol % on a nitrogen-free basis, which can be used as syngas components. The solid product has a large Brunauer–Emmett–Teller (BET) surface area of $278 \text{ m}^2 \text{ g}^{-1}$ and a large pore volume of $0.15 \text{ cm}^3 \text{ g}^{-1}$. The applications of plasma techniques used are widespread in treating hazardous wastes and flare gas,¹² such as polypropylene,¹³ municipal solid waste,¹⁴ electrosludge,¹⁵ polychlorinated biphenyls (PCBs),¹⁶ carbonaceous waste,¹⁷ waste tires,¹⁸ benzene,¹⁹ 1,2-dichloroethane (DCE),²⁰ and halogenated hydrocar-

bons.²¹ In other applications, the RF plasma technique can be applied to the (1) manufacture of SiO_2 nanofiber,²² nanocrystalline ZnO film,²³ a CeO_2 -buffer layer,²⁴ nanotubes,²⁵ and fullerenes,²⁶ (2) reduction of SO_2 to element S (with CH_4 as the reductant),²⁷ (3) transformation of CH_4 into syngas,²⁸ and (4) generation of H_2 .²⁹ The thermal plasma pyrolysis of biomass for the production of energy and chemicals has seldom been studied even in laboratory investigations because of technical difficulties or applied for economic reasons.¹¹ Today, one of the main factors that restricts the use of plasma-based methods is the cost of electrical energy. The crucial element is the operation and maintenance cost of the plasma generator and reactor. The ways to increase the efficiency of the process are also very important. In order to overcome parts of this problem, the need for electric energy for plasma technology may be supplied partly from the power generated via the use of the product of syngas. Tendler et al.³¹ addressed the fact that the energies stored in syngas are all higher than the energy consumption from the operation of plasma technology (a plasma torch). On the other hand, the investment costs of plants of plasma torches are typically 30–50% lower than those of incinerators of the same capacity.³⁰ Another effect of the operation cost for a plasma torch application is the cost of feedstock. Therefore, the best choice of feedstock is waste from biomass or waste organic materials.

Experimental Section

The schematic diagram of the RF plasma thermolysis system is shown in Figure 1. The RF plasma reactor consists of a quartz tube with an outer diameter of 50 mm, a wall thickness of 2 mm, and a length of 500 mm. The electrodes are two pieces of copper arcs with a length of 320 mm, which are fixed and covered around the outside of the quartz tube with a gap between two electrodes. The length of the RF plasma producing zone is about 320 mm. The working gas is chosen as N_2 with a purity of 99.99%. Its flow rate (Q) of working gas through the drying tube is controlled via a mass flow controller (Brooks, 5850E, USA). In all experiments, Q is kept at 200 mL min^{-1} . In order to hold the vacuum in the plasma reactor, the sample is fed by a continuous feeding apparatus with two valves open and closed exchanged. The cold trap with a temperature of 298 K and a volume of 3 L is installed after the RF plasma thermolysis reactor to collect the liquid products. In order to maintain a suitable degree of vacuum in the plasma reactor, the switch valves and the vacuum meter (Terranova, model 906A) are installed. Three digital thermometers (TFC 305A, type K) are used to detect the temperatures of the RF plasma reactor and the inlet and outlet of the cold trap. The RF plasma power supply

(7) Demirbas, A. *Energy Sources* **2005**, *27*, 823–830.
 (8) Zhao, Z. L.; Huang, H. T.; Wu, C. Z.; Li, H. B.; Chen, Y. *Chem. Eng. Technol.* **2001**, *24*, 197–199.
 (9) Merida, W.; Maness, P. C.; Brown, R. C.; Levin, D. B. *Int. J. Hydrogen Energy* **2004**, *29*, 283–290.
 (10) Yaman, S. *Energy Convers. Manage.* **2004**, *45*, 651–671.
 (11) Tang, L.; Huang, H. *Energy Fuels* **2005**, *19*, 1174–1178.
 (12) Mollah, M. Y. A.; Schennach, R.; Patscheider, J.; Promreuk, S.; Cocco, D. L. *J. Hazard. Mater.* **2000**, *79*, 301–320.
 (13) Guddeti, R. R.; Knight, R.; Grossmann, E. D. *Plasma Chem. Plasma Process.* **2000**, *20*, 37–64.
 (14) Katou, K.; Asou, T.; Kurauchi, Y.; Sameshima, R. *Thin Solid Films* **2001**, *386* (2), 183–188.
 (15) Ramachandran, K.; Kikukawa, N. *IEEE Trans. Plasma Sci.* **2002**, *30*, 310–317.
 (16) Kim, S. W.; Park, H. S.; Kim, H. J. *Vacuum* **2003**, *70*, 59–66.
 (17) Nishikawa, H.; Ibe, M.; Tanaka, M.; Ushio, M.; Takemoto, T.; Tanaka, K.; Tanahashi, N.; Ito, T. *Vacuum* **2004**, *73*, 589–593.
 (18) Tang, L.; Huang, H. *J. Anal. Appl. Pyrolysis* **2004**, *72*, 35–40.
 (19) Shih, S. I.; Lin, T. C.; Shih, M. L. *J. Hazard. Mater.* **2004**, *116*, 239–248.
 (20) Li, C. T.; Yang, R. B.; Shih, M. L.; Chen, C. Y.; Hsieh, L. T. *J. Chem. Technol. Biotechnol.* **2003**, *78*, 817–823.

(21) Watanabe, T.; Shimbara, S. *High Temp. Mater. Process.* **2003**, *7*, 455–474.
 (22) Zhang, G.; Kataphinan, W.; Teye-Mensah, R.; Katta, P.; Khatri, L.; Evans, E. A.; Chase, G. G.; Ramsier, R. D.; Reneker, D. H. *Mater. Sci. Eng.: B* **2005**, *116*, 353–358.
 (23) Lee, J.; Gao, W.; Li, Z.; Hodgson, M.; Metson, J.; Gong, H.; Pal, U. *Appl. Phys. A: Mater. Sci. Process.* **2005**, *80*, 1641–1646.
 (24) Sohma, M.; Yamaguchi, I.; Tsukada, K.; Kondo, W.; Kamiya, K.; Mizuta, S.; Manabe, T.; Kumagai, T. *IEEE Trans. Appl. Superconductivity* **2005**, *15*, 2699–2702.
 (25) Lee, K. Y.; Ikuno, T.; Tsuji, K.; Ohkura, S.; Honda, S.; Katayama, M.; Oura, K.; Hirao, T. *J. Vac. Sci. Technol. B* **2003**, *21*, 1437–1441.
 (26) Jenkins, G. M.; Holland, L. R.; Maleki, H.; Fisher, L. *Carbon* **1998**, *36*, 1725–1727.
 (27) Tsai, C. H.; Lee, W. J.; Shih, M. L.; Chen, C. Y.; Tsai, P. J. *AIChE J.* **2004**, *50*, 524–529.
 (28) Tsai, C. H.; Hsieh, T. H. *Ind. Eng. Chem. Res.* **2004**, *43*, 4043–4047.
 (29) Li, H. Q.; Zou, J. J.; Liu, C. J. *Prog. Chem.* **2005**, *17*, 69–77.
 (30) Shie, J. L.; Chang, C. Y.; Lin, J. P.; Lee, D. J.; Wu, C. H. *J. Chin. Inst. Environ. Eng.* **2001**, *11*, 307–316.
 (31) Tendler, M.; Rutberg, P.; van Oost, G. *Plasma Phys. Control. Fusion* **2005**, *47*, A219–A230.

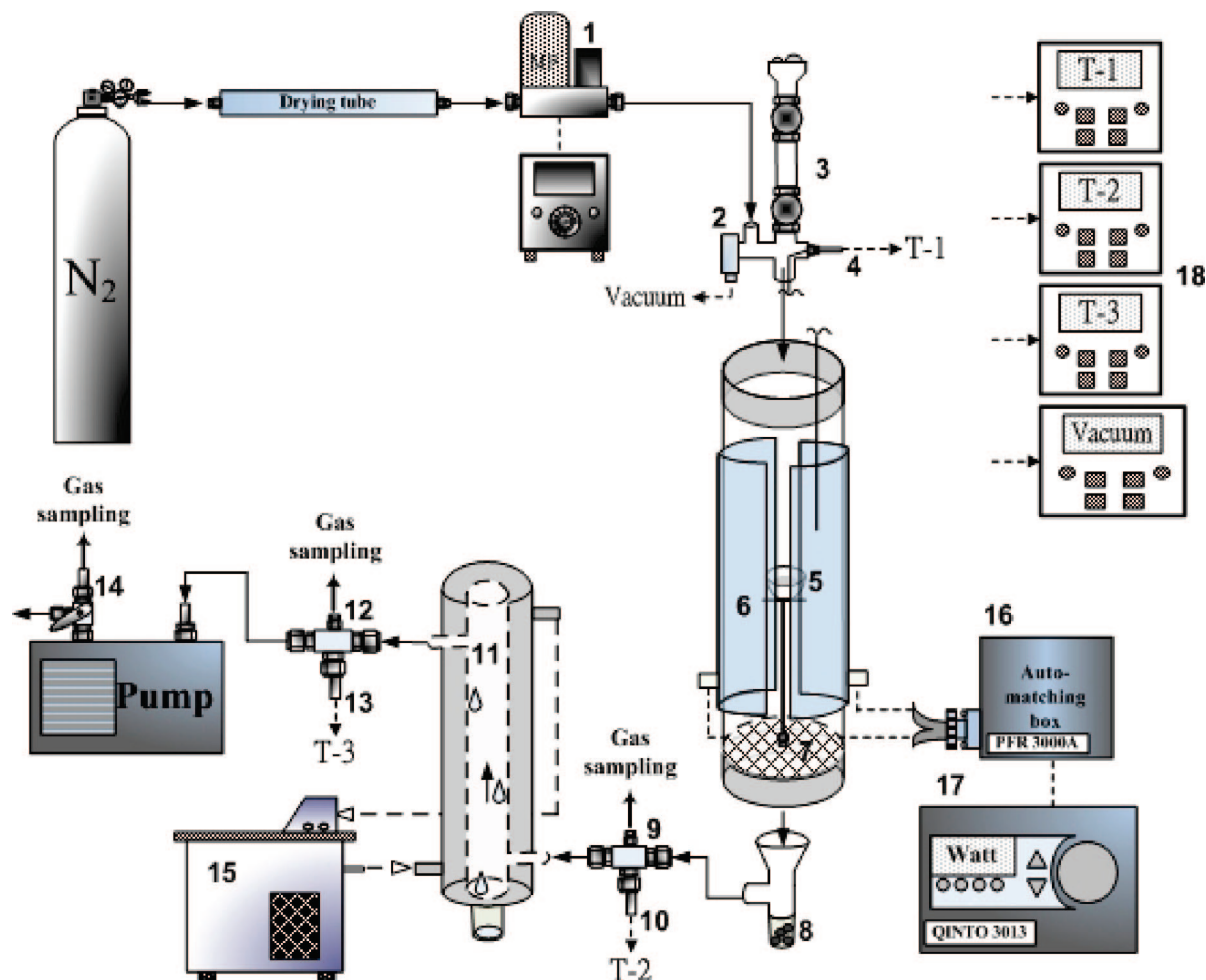


Figure 1. Schematic diagram of the RF plasma thermolysis system: (1) mass flow rate controller; (2) vacuum meter; (3) continuous feeding apparatus; (4, 10, and 13) thermocouples; (5) crucible and its support; (6) copper electrodes; (7) stainless steel net (25 mesh and 0.71 mm); (8) solid product storage; (9, 12, and 14) gas product samplers; (11) condenser and liquid product collector; (15) circulating thermostat; (16) automatching box; (17) RF plasma power supply; (18) digital monitors.

(Huettinger, QINTO 3013, Germany) and automatching box (Huettinger, PFM3000A, Germany) can provide a maximum voltage of 2000 W and RF frequency of 13.56 MHz. The temperatures are controlled from 300 to 950 K with the input power of 137 to 591 W under the net pressure of 1 torr. In this study, the RF plasma thermolysis reactor is used for pyrolyzing the biomass waste of rice straw. The reactor used can be adjusted for batch or continuous operation. In the batch experiment, the sample of rice straw was put in the crucible, which was supported by the stainless steel net. After the completion of experiment, the residual solid product in the crucible was weighed. Three replicates were performed.

The thermogravimetric system (Shimadzu TGA-51) used for the kinetic studies is shown schematically in Figure 2 and is the same as that used in the previous study.^{32–37} It mainly consists of electrobalance and furnace units. Some specifications of the balance mechanism are the following: balance type of taut band, capacity of 10 g, resolution of 1 μg , accuracy of 1% of each measuring range. The furnace unit has an electrically heated reaction tube of

20 mm in inner diameter and 170 mm in length. A sample (6 ± 0.2 mg) is placed in a Pt cell of 6 mm in diameter and 2.5 mm in depth. The cell is then put on a Pt sample pan that is hung by a quartz suspension wire (155 mm long) and connected to the balance mechanism. The temperatures of the furnace reaction tube are in the range 373–1073 K and controlled by a chromel–alumel thermocouple placed 1–2 mm below the Pt sample pan. The nitrogen gas with a known flow rate (e.g., 50 and 200 $\text{cm}^3 \text{min}^{-1}$, 101 kPa (1 atm), and 293 K) is first introduced into the balance mechanism and then to the furnace reaction tube for at least 2 h for purging purposes. After 2 h, the furnace unit is set at a specific heating rate (HR; 5 and 75 K min^{-1}). Meanwhile, the data acquisition unit, with sampling intervals of 1 s, is processing throughout the entire run. The effluent gas is cold-trapped at 298 K and then collected by a sample bag or vented to a fume hood. When the run is finished, the nitrogen gas is kept flowing until the temperature of the system is below 373 K.

The elemental analyses for the samples were made employing a Perkin-Elmer, Norwalk, CT2400 elemental analyzer with 0.3 wt % accuracy. The elements of C, H, and N were analyzed via Heraeus CHN-O-RAPID, and S and Cl analyzed via Tacussel Coulomax 78 automatic coulometric titrator. The heavy metals were measured using inductively coupled plasma atomic emission spectroscopy (ICP/AES; Jarrel-Ash, ICAP 9000). The mass of sample used for the digestion experiment was 0.5 g. For the purposes of analysis, the samples were pretreated by mixing with 2 mL concentrated HNO_3 , 0.5 mL HClO_4 , and 1 mL HF and then digested at 443 K for 6 h. The heating values of samples were measured by the adiabatic bomb calorimeter (O.S.K., 150 vacuum

(32) Moustakas, K.; Fatta, D.; Malamis, S.; Haralambous, K.; Loizidou, M. *J. Hazard. Mater.* **2005**, *B123*, 120–126.

(33) Shie, J. L.; Chen, Y. H.; Chang, C. Y.; Lin, J. P.; Lee, D. J.; Wu, C. H. *Energy Fuels* **2002**, *16*, 109–118.

(34) Shie, J. L.; Chang, C. Y.; Lin, J. P.; Lee, D. J.; Wu, C. H. *J. Chin. Inst. Environ. Eng.* **2002**, *12*, 65–76.

(35) Shie, J. L.; Lin, J. P.; Chang, C. Y.; Lee, D. J.; Wu, C. H. *J. Chin. Inst. Environ. Eng.* **2002**, *12*, 363–371.

(36) Wu, C. H.; Chang, C. Y.; Tseng, C. H.; Lin, J. P. *J. Chin. Inst. Environ. Eng.* **2003**, *13*, 67–76.

(37) Huang, H. C.; Chang, C. Y.; Chen, Y. H.; Shie, J. L.; Lin, J. P.; Wu, C. H. *J. Chin. Inst. Chem. Eng.* **2004**, *35*, 623–632.

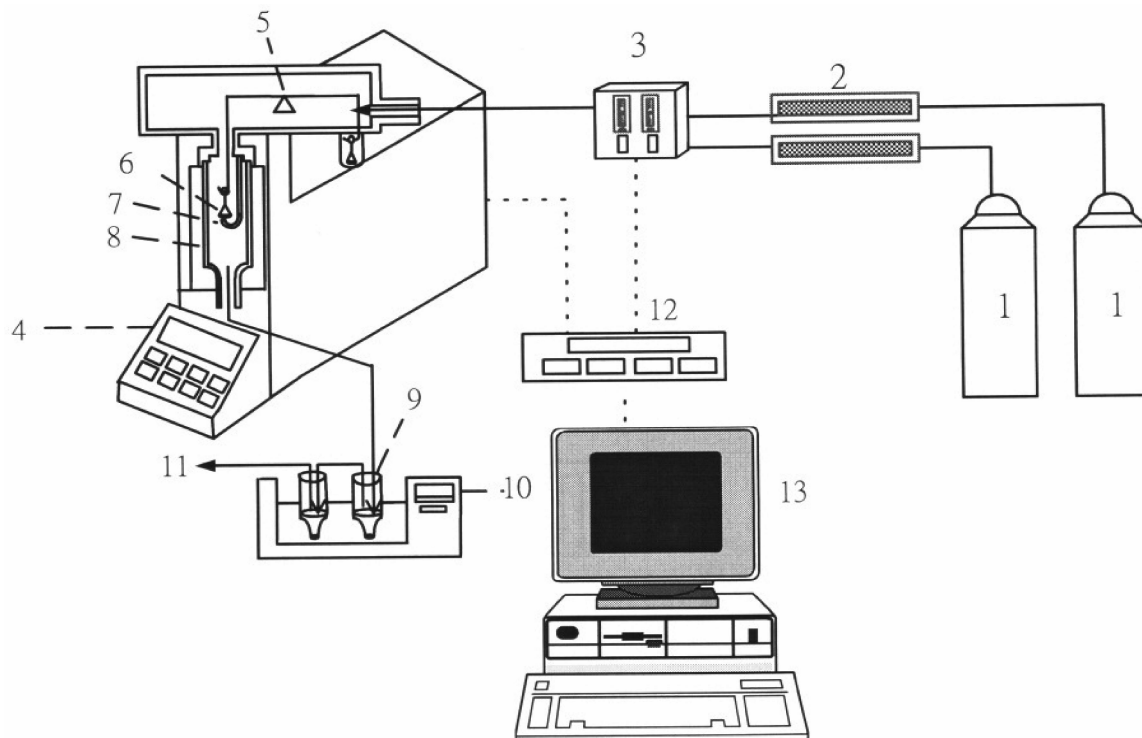


Figure 2. Experimented system of traditional thermolysis system using electric–thermal heating: (1) nitrogen; (2) drying tube; (3) mass flow controller; (4) control board; (5) electrobalance; (6) sample disk; (7) thermocouples; (8) furnace; (9) condenser tubes; (10) constant temperature bath; (11) to sample bag; (12) data acquisition; (13) personal computer.^{30–35}

flask oxygen bomb calorimeter). The proximate analysis included moisture, combustible, and ash. The moisture was obtained from the difference between the original mass and the mass after drying for 2 h at 378 ± 5 K. The combustible content was measured from the difference between the mass dried for 2 h at 378 ± 5 K and the final mass burned for 3 h at 1273 ± 50 K. The final mass was the ash. The thermogravimetric analyzer (TGA) used in this study is the Shimadzu TGA-51 with 1% accuracy for recording the variation in mass from 373 to 1123 K.

Results and Discussion

Pretreatment and Characteristics of the Rice Straw. The biomass used in this study was rice straw. The rice straw sample was exposed under the sunlight for 10 days in order to get rid of the surface water. Then, the sample was broken by spiral breaker and sieved into 30–40 mesh (0.6–0.425 mm) and dried in a recycle ventilation drier for 24 h at 378 K before use. The results of proximate, heating value, and elemental analyses of rice straw are listed in Table 1. The elemental analyses of the metal content of rice straw are presented in Table 2. In Table 1, the combustible value of rice straw is 79.8 wt % and the heating value is $4042 \text{ kcal kg}^{-1}$, supporting the use of rice straw as an energy source. The contents of C and O of rice straw are 39.6 and 53.7 wt %, respectively. It is obvious that the sulfur, chloride, and nitrogen are rare and can be neglected in the utilization of rice straw. The major mineral matter contents are Si, Al, Na, and Mg, and their values are 54803, 1113, 1030, and 990 ppmw, respectively. The total mineral matter is about 59619.6 ppmw. From Table 2, the total value of oxide compounds of mineral matter is about 12.5 wt % (125074.8 ppmw) and is near with that of ash (11.7 wt %). The results support that most of the biomasses have similar properties and offer the main advantage of using biomass for energy and

Table 1. Some Properties of Rice Straw Used in This Study

item	property
proximate analysis (wt %)	
moisture	8.5 (0.30) ^a
combustible	79.8 (0.90)
ash	11.7 (1.15)
heating value of dry basis (kcal kg^{-1})	4,042
Elemental Analyses (dry basis, wt %)	
C	39.6 (0.23)
H	5.8 (0.32)
N	0.7 (0.20)
O	53.7 ^b (balance)
S	0.2 (0.02)
Cl	0.1

^a Numbers in parentheses are standard deviations (σ_{n-1}). ^b Including mineral matter.

resources production from pyrolysis.³⁸ The utilization of biomass for energy generation also assists the reduction of CO_2 and SO_2 emissions for preventing the greenhouse effect and acid rain.³⁹

The residual mass fraction (M) of rice straw with respect to the initial mass during pyrolysis by TGA is expressed on a normalized basis as

$$M = W/W_0 \quad (1)$$

where W and W_0 are the present and initial masses of sample, respectively. The modified residual mass fraction (M_c) with respect to the combustible mass of sample is defined as

$$M_c = (W - W_{\text{ash}})/(W_0 - W_{\text{ash}}) \quad (2)$$

where W_{ash} is the mass of ash in the sample. The variation of M with reaction temperature (T_r) with HR of 5 K min^{-1} is

(38) Sharma, R. K.; Bakhshi, N. N. *Can. J. Chem. Eng.* **1991**, *69*, 1071–1081.

(39) Liang, X. H.; Kozinski, J. A. *Fuel* **2000**, *79*, 1477–1486.

Table 2. Mineral Matter Analysis of Rice Straw (Dry Basis) Used in This Study

major metal ppmw ^a	Si	Al	Na	Mg	Ca	P	Mn	Fe	Zn	Sr	Cu	Ba
dry basis	54803	1113	1030	990.0	772.0	325.0	259.5	258.1	32.3	11.4	10.4	6.8
oxide compound	117435 (SiO ₂)	2102 (Al ₂ O ₃)	1388 (Na ₂ O)	1642 (MgO)	1081 (CaO)	576.6 (P ₄ O ₆)	410 (MnO ₂)	368.7 (Fe ₂ O ₃)	40.2 (ZnO)	13.5 (SrO)	13.0 (CuO)	7.6 (BaO)
major metal ppmw ^a	Cr	Ni	Pb	Cd	Co	Se	As	Hg	B	Ag	total	
dry basis	4.2	3.0	0.6	0.2	0.1	ND	ND	ND	ND	ND	59619.6	
oxide compound	5.5 (CrO)	3.8 (NiO)	0.6 (PbO)	0.2 (CdO)	0.1 (CoO)	ND	ND	ND	ND	ND	125074.8	

^a ppmw: ppm in wt/wt.

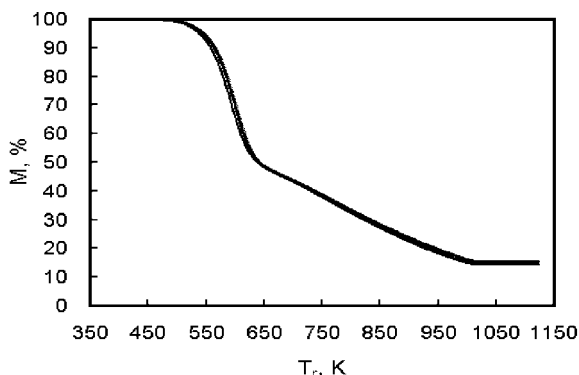


Figure 3. M vs T_r for the pyrolysis of rice straw via TGA: HR 5 K min^{-1} ; W_0 6 \pm 0.2 mg; d_p 0.425–0.6 mm; carrier gas N_2 ; Q 50 mL min^{-1} ; $M = W/W_0$; W , W_0 present and initial masses of sample; T_r reaction temperature; HR heating rate; d_p sample size; Q flow rate of inlet carrier gas; replication 3.

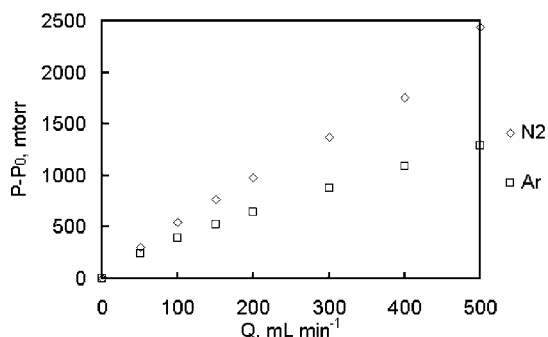


Figure 4. Net pressure ($P - P_0$) of N_2 (\diamond) and Ar (\square) at various Q values in the RF plasma reactor. P: Final pressure. P_0 : Initial pressure (89 mtorr). Setting of exhaust flow rate of vacuum pump: 40 L min^{-1} . R^2 for the cases of N_2 and Ar: 0.9922 and 0.9843.

illustrated in Figure 3. The pyrolytic reaction is significant in the range 550–650 K. There are two major reaction steps. The value of M at 1000 K is about 15 wt %, which is close to the ash content of rice straw ($= 11.7/(79.8 + 11.7) = 14.4$ on a dry basis). Therefore, the plateau temperature (T_p) for the pyrolysis of rice straw using RF plasma conducted in this study is set at the middle of the second step (783 ± 10 K) to ensure an acceptable reaction rate (R_r) of rice straw.

Operating Procedure and Characteristics of the RF Plasma Thermolysis Reaction. The effects of system parameters on the performance of RF plasma thermolysis of rice straw were examined. These include types of carrier gas, Q , net pressure ($P - P_0$) in the reactor, loading power (P_{WL}), reaction time (t), and T_r . P is the final pressure, while P_0 is the initial pressure under vacuum. P_{WL} can be online measured and recorded via the RF plasma power supply device. The net pressures ($P - P_0$) of N_2 and Ar in the RF plasma reactor at various values of Q are shown in Figure 4. For the pyrolysis experiments that followed using RF plasma, Q of N_2 or Ar was set at 200 mL min^{-1} and the net pressures of N_2 and Ar (with $P_0 = 89$ mtorr) were 1.00 ± 0.2 and 0.66 ± 0.2 torr,

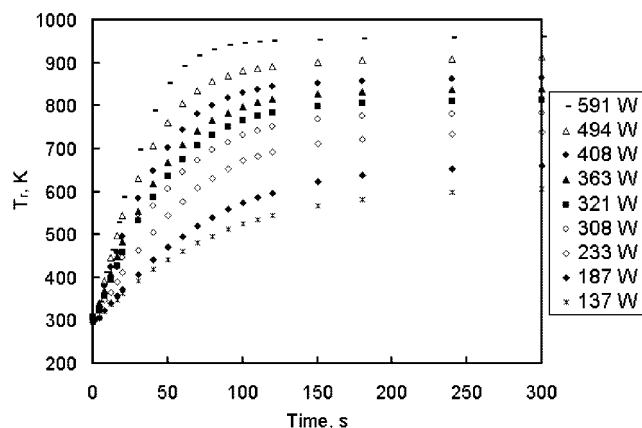


Figure 5. Time variation of T_r at various loading powers (P_{WL}) in the RF plasma reactor. $P_{WL} = P_{WI} - P_{WR}$; P_{WI} , P_{WR} powers supplied and reflected; carrier gas N_2 ; Q 200 mL min^{-1} ; net pressure 1.00 ± 0.2 torr; initial or room temperature (T_0) 298 ± 5 K.

respectively. The low values of the net pressures ensure gas flowing through the plasma thermolysis system with no leakage problem in experiments.

For temperature control, the time variations of T_r at various P_{WL} are shown in Figure 5. P_{WL} is the loading power used for the generation of RF plasma. It is equal to the input power (P_{WI}) minus reflected power (P_{WR}). P_{WI} is the power supplied from the RF plasma power supply, and P_{WR} is the useless power producing the wasted electromagnetic wave from reflection. Figure 6 shows P_{WL} vs T_p and HR in the RF plasma reactor. The values of HR and T_p are directly related to P_{WL} with a higher P_{WL} giving higher HR and T_p values. Obviously, HR can reach about 400 K min^{-1} at a P_{WL} of 600 W. According to Figure 5, the characteristics of the RF plasma thermolysis reactor with the working gas N_2 indicate that as P_{WL} increases from 137 to 591 W, the T_p of plasma increases from 607 to 954 K. The corresponding T_p at various values of P_{WL} are 607 K at 137 W, 661 K at 187 W, 738 K at 233 W, 784 K at 308 W, 810 K at 321 W, 833 K at 363 W, 853 K at 408 W, 901 K at 494 W, and 954 K at 591 W, respectively. The corresponding t_{HP} values to reach T_p values of 607 and 954 K are about 5 and 2 min, respectively. Thus, a higher P_{WL} gives a higher T_p with a shorter t_{HP} . The values of heating times t_{HS} with P_{WL} values of 308, 363, and 591 W to reach a setting temperature T_S at 783 K are about 5, 1.5, and 0.67 min, respectively. Again, a higher P_{WL} needs a shorter t_{HS} to reach the same T_S .

Comparison of Performances of Thermolysis Using RF Plasma and Traditional Methods. The performances of RF plasma thermolysis and traditional thermolysis of rice straw were compared. For comparison, the initial weight W_0 and sample size (d_p) of rice straw, Q of N_2 , and T_p were controlled at the same conditions for the two thermolysis methods with W_0 of 100 ± 10 mg, d_p of 30–40 mesh (0.6–0.425 mm), Q of 200 mL min^{-1} of N_2 , and T_p of 783 ± 10 K, respectively. The major difference between these two cases is their heating methods.

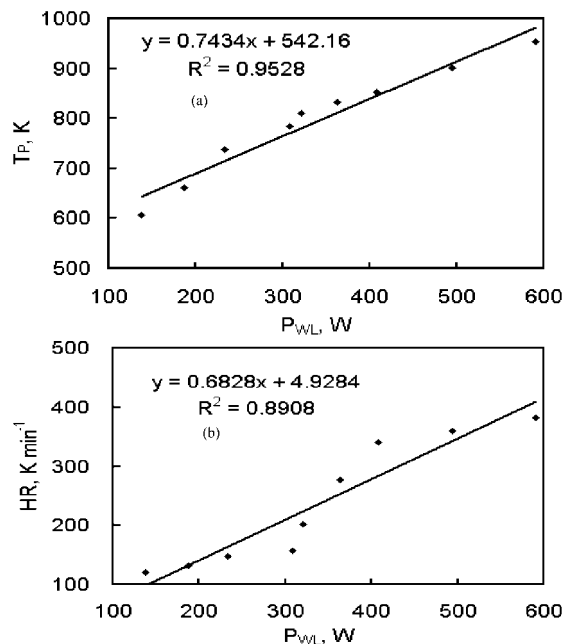


Figure 6. Loading power (P_{WL}) vs plateau temperature (T_p) and heating rate (HR) in the RF plasma reactor. $P_{WL} = P_{WI} - P_{WR}$; P_{WI} , P_{WR} powers supplied and reflected; carrier gas N_2 ; Q 200 mL min^{-1} ; net pressure 1.00 ± 0.2 torr; initial or room temperature (T_0) 298 ± 5 K. (a) P_{WL} vs T_p . (b) P_{WL} vs HR.

The RF plasma reactor produces plasma with ionization gas to heat the rice straw while the traditional furnace uses electric-thermal energy for heating the rice straw. The operating parameter of P_{WL} for reaching T_p of 783 K in the RF plasma reactor is 308 ± 4 W. For the comparison, the HR of a traditional furnace is set at the highest limited value of 70–75 $K min^{-1}$ for reaching a T_p of 783 K. Under the highest HR of the traditional heating method, the input power is near 1000 W. Therefore, the input power of RF plasma is lower than that of TGA in this study. The conditions of the traditional heating method are near the RF plasma reactor, such as plateau temperature (T_p) 783 ± 10 K, initial mass of sample (W_0) 100 ± 10 mg, sample size (d_p) 0.425–0.6 mm, carrier gas (Q) of N_2 : 200 mL min^{-1} , initial or room temperature (T_0) 298 ± 5 K. The only different condition is the heating rate (95 $K min^{-1}$ of RF plasma and 70–75 $K min^{-1}$ of the traditional heating method). This is because of the power limited of traditional heating method with maximum power of 1000 W at highest heating rate of 70–75 $K min^{-1}$.

From Figures 7 and 8, the values of t_{HP} of RF plasma thermolysis and traditional thermolysis are 5 and 6–7 min, respectively. At the reaction time of 90 min, the values of M_c of rice straw for the pyrolyses with RF plasma and traditional methods are about 50 and 42.6 wt %, respectively. The corresponding thermolysis efficiencies of the RF plasma and TGA methods are 50 and 57.4 wt %, respectively. Note that the HRs of pyrolyses for the RF plasma and traditional methods are 95 and 70–75 $K min^{-1}$, respectively. When we focus on M_c at 90 min, the thermolysis efficiency of traditional thermolysis method (57.4%) is slightly higher than that of the RF plasma thermolysis method (50%). However, if we note M_c and the corresponding T_r at the same time scale, we can find something interesting. In the RF plasma thermolysis system, M_c decreases about 3% only as T_r increases from T_0 to T_p while it retains 97% for further thermolysis at T_p counting for a decomposition of rice straw of 47% ($= 50\% - 3\%$). The R_r of an RF plasma thermolysis system is about 0.55 wt % min^{-1} at T_p . As for the

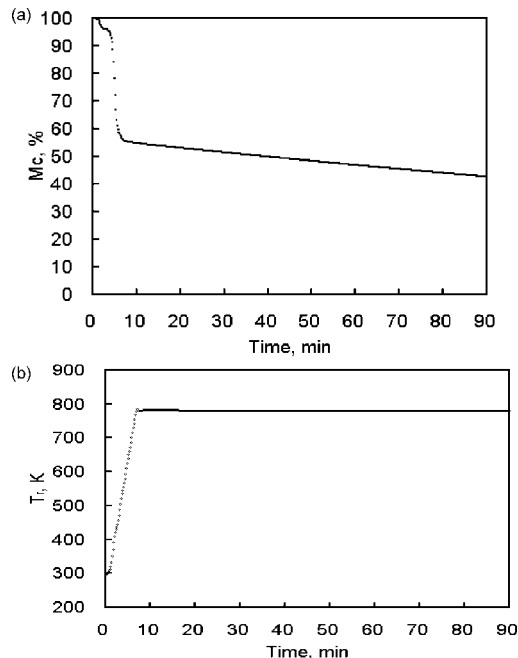


Figure 7. Time variations of M_c and T_r for the pyrolysis of rice straw via the traditional heating method at $T_p = 783$ K: HR 70–75 $K min^{-1}$; T_p 783 ± 10 K; W_0 100 ± 10 mg; d_p 0.425–0.6 mm; carrier gas N_2 ; Q 200 mL min^{-1} ; T_0 298 ± 5 K; replication 4. (a) M_c vs time. (b) T_r vs time.

Table 3. Fractions^a of the Products of Combustible Solid Remained, Liquid, and Gas from the Thermolysis of Rice Straw Using RF Plasma and Traditional Methods at $T_p = 783$ K with a Reaction Time of 90 min

thermolysis/product	combustible solid remained (M_c ; wt %)	liquid products (wt %)	gas product (wt %)
RF plasma thermolysis	50.0	0	50.0
traditional thermolysis	42.6	1.5	55.9
Tang and Huang ⁴²	34 (11.6–67.5) ^b		66

^a Ash free basis, i.e., with respect to the initial mass of sample excluding ash ($W_0 - W_{ash}$). ^b Range for different operating conditions.

traditional thermolysis system, M_c decreases from the initial value (M_{c0}) of 1 to 0.56 as T_r increases from T_0 to T_p in the heating stage, yielding a decomposition of 44% ($= (1 - 0.56)/1$) with respect to M_{c0} . For further thermolysis at constant T_p , M_c reduces to 0.426 at 90 min giving an overall decomposition of 57.4% ($= (1 - 0.426)/1$) with respect to M_{c0} . Thus, the incremental net contribution of decomposition during thermolysis at constant T_p is only 13.4% ($= 57.4\% - 44\%$). Therefore, the R_r of a traditional thermolysis system is 0.16 wt % min^{-1} at T_p . Comparison at T_p , the R_r of the RF plasma thermolysis system is 3.44 times higher than that of a traditional thermolysis system. The enhancement effect on R_r of an RF plasma thermolysis system is very obvious. Higher R_r will decrease reaction time and energy demand.

Further, for a fair comparison of the two methods, we also have to note the tar content in the gas produced from the pyrolysis of biomass, which always plays an important role for the operation of the thermolysis process. A high tar content may cause the corroding problem of the device and increase the need for the further treatment of the gas produced. Although the composition of syngas in the gas product is not available, however, plasma technologies for the thermolysis of biomass would not only yield high concentrations of syngas but also result in low concentrations of tar in a gas phase, mostly below 10 mg Nm^{-3} as noted by Hlina et al.⁴⁰

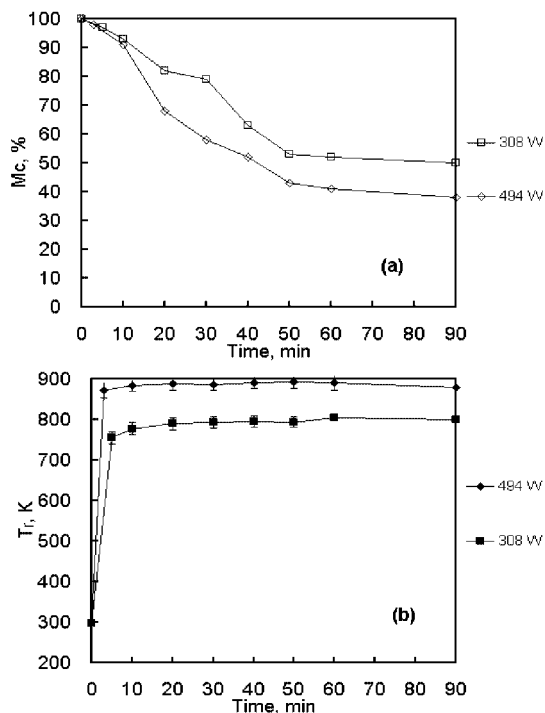


Figure 8. Time variations of M_c and T_r for the pyrolysis of rice straw via RF plasma method at $T_p = 783$ and 883 K with $P_{WL} = 308 \pm 4$ and 494 ± 4 W, respectively: HR 95 and 190 K min^{-1} ; $T_p 783 \pm 10$ and 883 ± 10 K; $W_0 100 \pm 10$ mg; $d_p 0.425\text{--}0.6$ mm; carrier gas N_2 ; $Q: 200 \text{ mL min}^{-1}$. P-P₀: 1.00 ± 0.2 torr. $T_0: 298 \pm 5$ K. (a) M_c vs. time, (b) T_r vs. time.

Fractions of Products of Combustible Solid Remained, Liquid, and Gas. Table 3 lists the fractions of the products of combustible solid remained (M_c), liquid, and gas from the thermolysis via RF plasma and traditional methods which clearly indicates the differences between these two heating methods. The values are expressed on an ash free basis with respect to the initial mass of sample excluding ash ($W_0 - W_{\text{ash}}$). Noting that the sample of rice straw was dried before use, we can conclude that the liquid products are the tar and some complex compounds of high boiling point.² Pütin et al.⁴¹ studied the pyrolysis of rice straw to estimate the effect of pyrolysis conditions on product yields and bio-oil composition. The subfractions of bio-oil from pyrolysis of rice straw are 27.48 wt % aliphatic, 11.46 wt % aromatic, 31.28 wt % ester, and 29.78 wt % polar. From the gas-liquid chromatogram of the *n*-pentane, i.e. aliphatic subfraction for bio-oil, the straight chain alkanes and alkenes range between $\text{C}_9\text{--}\text{C}_{28}$ and the distribution of straight chain alkanes exhibits a maximum on the range of $\text{C}_{10}\text{--}\text{C}_{14}$. Tang and Huang⁴² used a laboratory-scale capacitive coupled radio-frequency (RF) plasma pyrolysis reactor to examine the characteristics of this RF plasma reactor and the products of fir sawdust gasification. It was founded that sawdust gasification using an input power of 1600–2000 W and a reactor pressure of 3000–8000 Pa produced gas consisting of H_2 (3.88–11.06 vol %), CO (5.21–14.82 vol %), CH_4 (1.38–2.48 vol %), CO_2 (1.51–5.05 vol %), and C_2 (1.5–3.92 vol %) as well as char. On average, the gas yield can reach 66 wt % of the sawdust feed, and the comparison with this study is listed in Table 3.

About 1.5 wt % liquid products were collected from the thermolysis using the traditional method. These products exist in the form of tar with very high viscosity and deposits on the

inner wall of condenser tubes. On the other hand, no liquid products were collected from the RF plasma thermolysis in this study. This may be contributed to the causes that only a small amount of rice straw (nearly 3%) was decomposed in the heating stage with temperature rise and that the energy species generated via RF plasma can enhance the decomposition of tar and complex compounds if they were produced.

From these findings, it is believed that the gaseous product obtained via thermolysis using RF plasma contains more hydrocarbons of low molecular weight than those using traditional electric-thermal heating. A further study on the characteristics of gas product would be helpful for supporting the above points.

Thermolysis via RF Plasma at Various Plateau Temperatures. Figure 8 shows the results of thermolysis of rice straw via RF plasma performed at two different heating conditions with T_p at 783 and 883 K, corresponding to P_{WL} values of 308 ± 4 and 494 ± 4 W, respectively. With P_{WL} values of 308 and 494 W, the RF plasma took about 5 and 3 min to raise the thermolysis temperature T_r from T_0 to 783 and 883 K with weight losses of rice straw of 3% and 2% in terms of M_c , respectively. Besides, at a reaction time of 90 min, the case with a P_{WL} of 494 W offered better decomposition than that of 308 W, with the decomposition efficiencies of 62% and 50%, respectively. Thus, a higher P_{WL} needs less time to raise T_r from T_0 to T_p and gives a better thermolysis efficiency.

Conclusions

1. RF plasma thermolysis offers a faster heating rate and can retain more residues of rice straw than the traditional thermolysis via electric-thermal heating at the same plateau temperature T_p .

2. RF plasma thermolysis has no corroding problem because no tar is formed, while traditional pyrolysis results in about 1.5 wt % of tar for the experimental conditions examined in this study.

3. The time for the RF plasma process to reach T_p is short, decreasing the formation of complex compounds from intermediate residues at various temperatures during the period of temperature rise. We can infer that the contents of gas products from the RF plasma thermolysis of rice straw are simpler with better quality than those from traditional thermolysis.

Acknowledgment. We express our sincere thanks to the National Science Council of Taiwan for the financial support, under the contract number NSC94-2218-E-002-070.

Nomenclature

d_p = sample size, mm
 HR = heating rate, K min^{-1}
 M = residual mass fraction, –
 M_c = modified residual mass fraction, –
 P = final pressure, torr
 P_0 = initial pressure, torr
 P_{WI} = input power, W
 P_{WL} = loading power, W
 P_{WR} = reflected power, W
 Q = flowrate of carrier gas, mL min^{-1}
 R_r = reaction rate, wt \% min^{-1}
 T_0 = initial or room temperature, K
 T_p = plateau temperature, K
 T_s = setting temperature, K
 T_r = reaction temperature, K
 t_H = heating time, min
 t_{HP} = value of t_H to reach T_p , min
 t_{HS} = value of t_H to reach T_s , min
 W = present mass of sample, mg
 W_0 = initial mass of sample, mg
 W_{ash} = mass of ash in sample, mg

(40) Hlina, M.; Hrabovsky, M.; Kopecky, V.; Konrad, M.; Kavka, T.; Skoblja, S. *Czech. J. Phys.* **2006**, *56*, B1179–B1184.

(41) Pütin, A. E.; Apaydm, E.; Pütin, E. *Energy* **2004**, *29*, 2171–2180.

(42) Tang, L.; Huang, H. *Fuel* **2005**, *84*, 2055–2063.