

Product distribution from solar pyrolysis of agricultural and forestry biomass residues



Rui Li ^a, Kuo Zeng ^a, José Soria ^b, Germán Mazza ^b, Daniel Gauthier ^a, Rosa Rodriguez ^c, Gilles Flamant ^{a,*}

^a Processes, Materials and Solar Energy Laboratory (PROMES-CNRS, UPR 8521), 7 Rue du Four Solaire, Odeillo 66120 Font-Romeu, France

^b Institute for Research and Development in Process Engineering, Biotechnology and Alternative Energies (PROBIEN, CONICET – UNCo), 1400 Buenos Aires St., 8300 Neuquén, Argentina

^c Chemical Engineering Institute, National University of San Juan, 1109 Libertador (O) Avenue, 5400 San Juan, Argentina

ARTICLE INFO

Article history:

Received 3 October 2015

Received in revised form

12 November 2015

Accepted 28 November 2015

Available online xxx

Keywords:

Solar pyrolysis

Agricultural by-product biomass

Forestry by-product biomass

Products' yield

Syngas

ABSTRACT

Solar pyrolysis of pine sawdust, peach pit, grape stalk and grape marc was conducted in a lab-scale solar reactor for producing fuel gas from these agricultural and forestry by-products. For each type of biomass, whose lignocellulose components vary, the investigated parameters were the final temperature (in the range 800 °C–2000 °C) and the heating rates (in the range 10–150 °C/s) under a constant sweep gas flow rate of 6 NL/min. The parameter influence on the pyrolysis product distribution and syngas composition was studied. The experimental results indicate that the gas yield generally increases with the temperature and heating rate for the various types of biomass residues, whereas the liquid yield progresses oppositely. Gas yield as high as 63.5wt% was obtained from pine sawdust pyrolyzed at a final temperature of 2000 °C and heating rate of 50 °C/s. This gas can be further utilized for power generation, heat or transportable fuel production.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Agricultural and forestry wastes had little interest for centuries, but in the last decades, with the concern of the energy community for their valorization, they started being considered as valuable feedstock for energy transformation. Nowadays, the conversion of agricultural by-products and wood into bio-fuels is largely concerned in many countries. Pyrolysis is one of the most attractive processes to convert biomass into bio-gas, bio-oil and bio-char [1].

However, pyrolysis requires extra energy input such as electrical heating source combustion of some non-condensables or of the char [2], thus reducing the energy conversion efficiency and causing environmental problems. This can be overpassed by using concentrated solar energy as the heat input for processing biomass into solar fuels [3]. Indeed, implementing of concentrated solar energy as heat source for the pyrolysis reactions can increase the energy conversion efficiency of the process and reduce its pollution discharge [4]. In this objective, a few researchers have used image furnace for simulating solar-driven carbonaceous materials

pyrolysis [5,6]. In these studies, the liquid products were the target or main products. However, in spite of the interest of using real solar furnace for biomass pyrolysis, published works related to such type of pyrolysis are scarce [7–9].

Lots of researches about biomass pyrolysis have been developed in the reactors heated by combustion of pyrolysis products, such as fluidized-bed [10–12], rotary kiln [13] and free fall reactors [14]. Some typical slow and fast pyrolysis reactors have been reviewed by Bridgwater AV [15]. An interesting pilot plant of flash pyrolysis was presented by Maniatis et al. [16] with the aim to produce bio-oil. The obtained oil yield was 45wt% which is compatible with our result, whereas their particle size is greater. Recent previous studies on traditional pyrolysis have shown that the most important parameters are the temperature and heating rate, since they determine the products distribution and properties [17,18]. Because primary tars easily crack into low molecular weight gases above approximately 500 °C [19], the liquid yield decreases and gas yield generally increases over this temperature [20]. The char yield initially decreases with rising temperature and then remains approximately constant above 600 °C [21]. Fast heating rate reduces the heat and mass transfer limitations, thus it favors bond–scission reactions and enhances the primary volatiles (tar

* Corresponding author.

E-mail address: gilles.flamant@promes.cnrs.fr (G. Flamant).

Table 1
Feedstock composition.

Biomass	Volatile materials (wt.%)	Water-content (wt.%)	Elements (wt.%)					Ash (wt.%)	Lignocelluloses (wt.%)		
			C	H	N	S	O		Cellulose	Hemicellulose	Lignin
Pine sawdust	82.4	7.19	50.93	6.02	0.1	0.05	42.9	0.53	42.96	19.99	26.8
Peach pit	79.12	7.2	53	5.90	0.32	0.05	39.14	1.59	31.58	21.02	27.53
Grape marc	68.54	10.92	52.91	5.93	1.86	0.03	30.41	8.81	15.31	4.96	37.97
Grape stalk	51.08	9.28	46.143	5.737	0.366	0	37.594	10.16	16.02	5.78	30.79

and gases) yield at cost of char yield [22]. The liquid and gases yields (CO, CO₂, H₂, CH₄ and C₂H₆) markedly increase when increasing the heating rate from 5 °C/min to 80 °C/min and the final pyrolysis temperature is 720 °C [23]. However, the liquid and gas yields do not improve with further heating rate increase, once heat and mass transfer limitations are overcome [24]. Various studies confirmed the obvious influence of biomass characteristics on the pyrolysis reactions and product yields. The compositional structures, which are mainly cellulose, hemicellulose and lignin, vary among the biomass feedstock [25], and they have different pyrolysis characteristics [26]. Cellulose relates to the wood strength and decomposes in the temperature range 240–350 °C and hemicellulose decomposes in the range 200–260 °C. Lignin is more difficult to dehydrate due to its physical and chemical properties, it decomposes in the temperature range 280–500 °C. On the one hand, cellulose turns generally into condensable vapor during pyrolysis,

whereas in contrast, hemicellulose produces more non-condensable gas and less tar. On the other hand, lignin degrades slowly and forms char.

Traditional pyrolysis is normally held below 1000 °C in flexibility-lacking reactors. Compared to such reactors, solar reactors are very interesting since they provide both a flexible heating temperature that ranges from 600 °C up to more than 2000 °C, and a flexible heating rate ranging from 5 °C/s to more than 450 °C/s, and this with a minimal energy cost. Therefore, more combustible gas products can be produced due to the advantages of direct solar pyrolysis (high temperature and fast heating rate). Then the pyrolysis gas products have a higher heating value than conventional gasification gases [27], and therefore, they can be utilized as fuel gas for power generation, heat or transportable fuel production.

There is another advantage with solar furnace. Traditional reactors such as TGA or tubular reactors present a slow heating rate

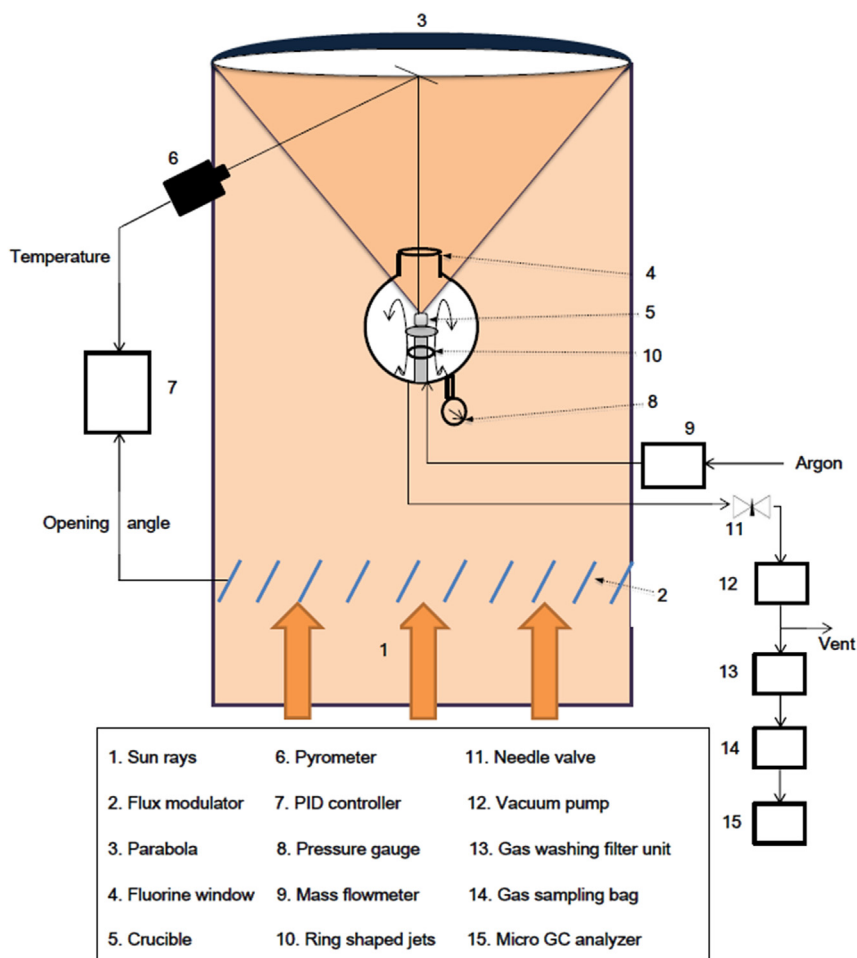


Fig. 1. Schematic of the solar pyrolysis experimental setup.

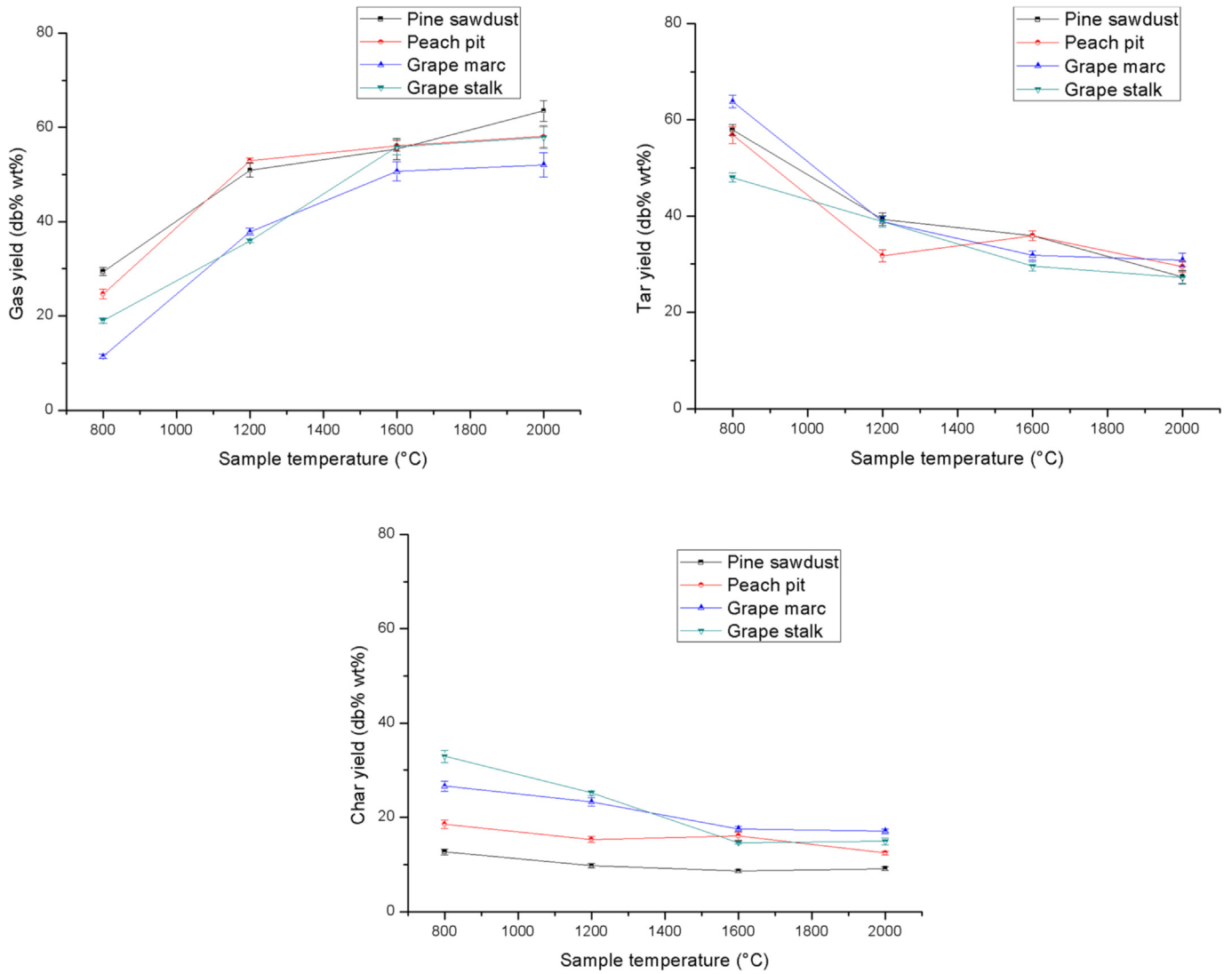


Fig. 2. Effect of final temperature on products yields from biomass pyrolysis at heating rate 50 °C/s.

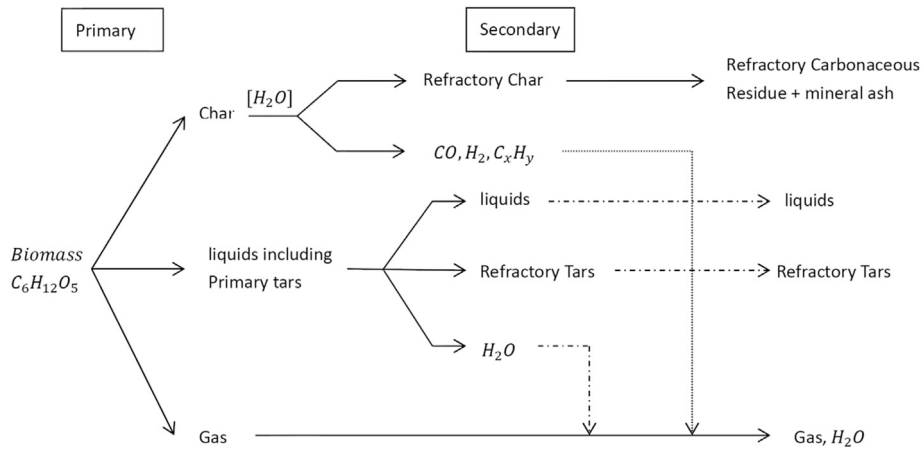


Fig. 3. Pyrolysis reaction scheme.

(10–100 K/min), oppositely to solar furnace with a flexible heating rate up to 450 K/s. Therefore, due to its high heating rate range, kinetic/thermal effects of solar furnace are very representative of fast pyrolysis.

The purpose of this study dealing with the thermal valorization of agricultural and forestry biomass wastes was to: (i) investigate the effects of temperature, heating rate and type of biomass on the product distribution and, gas composition obtained from solar pyrolysis; (ii) determine the optimum process parameters for maximum gas yield.

2. Experiment

2.1. Samples characterization

The raw materials considered in this experimental study were four kinds of biomass particles issued from Northern Patagonia (Argentina) from both forestry (pine sawdust) and agricultural industries (peach pit, grape stalk and grape marc in powder). The initial powder particle size is 100 μm , it is then compressed by a hydraulic compressor to form pellets of 5 mm height and 10 mm diameter. Some insulation is added around the crucible to reduce as

much as possible internal temperature gradients. The feedstock analyses are shown in Table 1. It can be seen that the pine sawdust contains more cellulose than the considered agricultural wastes, ranging from 1.5 fold (peach pit) to almost 3 fold (grape marc and grape stalk). The hemicellulose is about 5 times more concentrated in pine sawdust and peach pit than in the other types of biomass, whereas the lignin content is almost the same in all four biomass types. Finally, grape biomass contains a large amount of ash with respect to the two other feedstocks: about 9 wt% and 10 wt% for marc and stalk respectively. Experiments were run with cylindrical pellets (10 mm in diameter, 5 mm high), corresponding to approximately 0.3 g. A very thin carbon layer was previously deposited on the pellet surface in order to increase its absorptivity of the concentrated solar radiation. It also helps keeping the emissivity as 0.95 for sample temperature measurement by pyrometer. The carbon layer, agglomerated after heat treatment, was removed before char mass measurement.

2.2. Experimental setup and procedure

The experimental setup for solar pyrolysis of biomass is depicted in Fig. 1. In this vertical axis solar furnace, the sunlight is first

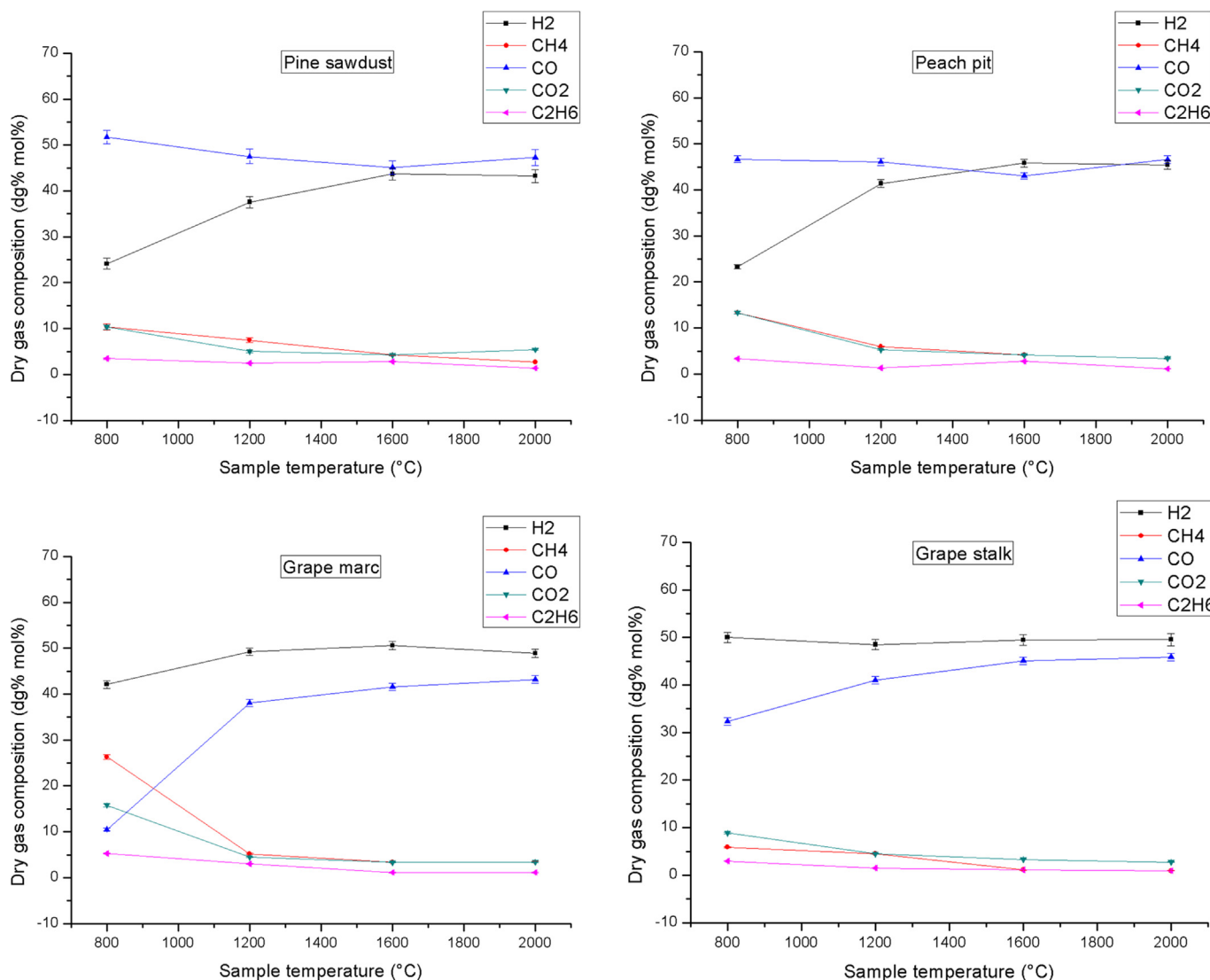


Fig. 4. Effect of final temperature on dry gas composition from biomass pyrolysis at heating rate 50 °C/s.

reflected by the heliostat and then concentrated by the 2 m dia. parabola. A transparent Pyrex balloon reactor with a 185 mm diameter (6 L volume), set at the focus, is swept with an argon flow controlled by a mass flowmeter (Bronkhorst, EL-FLOW[®]). The sweeping gas is used to provide an oxygen-free environment, and it also keeps the reactor walls clean. The sample temperature is measured online by a previously calibrated “solar-blind” optical pyrometer (KLEIBER monochromatic at 5.2 μm), which aims the sample through a fluorine window (transparent at this wavelength). The pyrometer was calibrated using blackbody radiation, and the sample temperature was validated by comparison with a K-type thermocouple measurement. The biomass pellet is set in a graphite crucible that is put on a 1-cm thick graphite foam layer for reducing as much as possible the temperature gradient in the biomass sample. Indeed, a water-cooled sample holder maintains the sample at the focus of the solar furnace. Another piece of graphite foam layer prevents radiative heat losses on the crucible sides. A shutter, made of composite carbon blades, is set on the reflected solar beam before its concentration. The target heating rate and final temperature are set on a PID controller, which controls the shutter opening based on the sample temperature

measured by the pyrometer. A needle valve set on the gas outlet tubing is used to regulate the reactor internal gas pressure constant as 0.52 bar. Finally, a vacuum pump and a gas washing filter unit are set downstream the needle valve. When samples are wanted, gaseous products are aspirated by a vacuum pump (the water content is removed by the gas washing filter), and collected in a sampling bag for analysis in a micro gas chromatograph. The gas sampling time is always 5 min throughout the pyrolysis process. On-time IR gas analysis of the exhaust gas has shown that the reaction is complete after this time for all experimental conditions.

For each experiment, the sample is weighted before and after thermal treatment to determine the mass of feedstock and char. The gas yield is calculated based on Ideal Gas Law and the gas composition determined by micro-gas chromatography. The liquid yield is then obtained from the mass balance. Finally, after each experiment, the reactor is cleaned by alcohol to eliminate any tar deposit on the walls. Each run was repeated at least 3 times for better accuracy, and the error was always less than 5%. Therefore, when plotting experimental results in this paper, mean values are marked with corresponding error bars as measure of the plot accuracy.

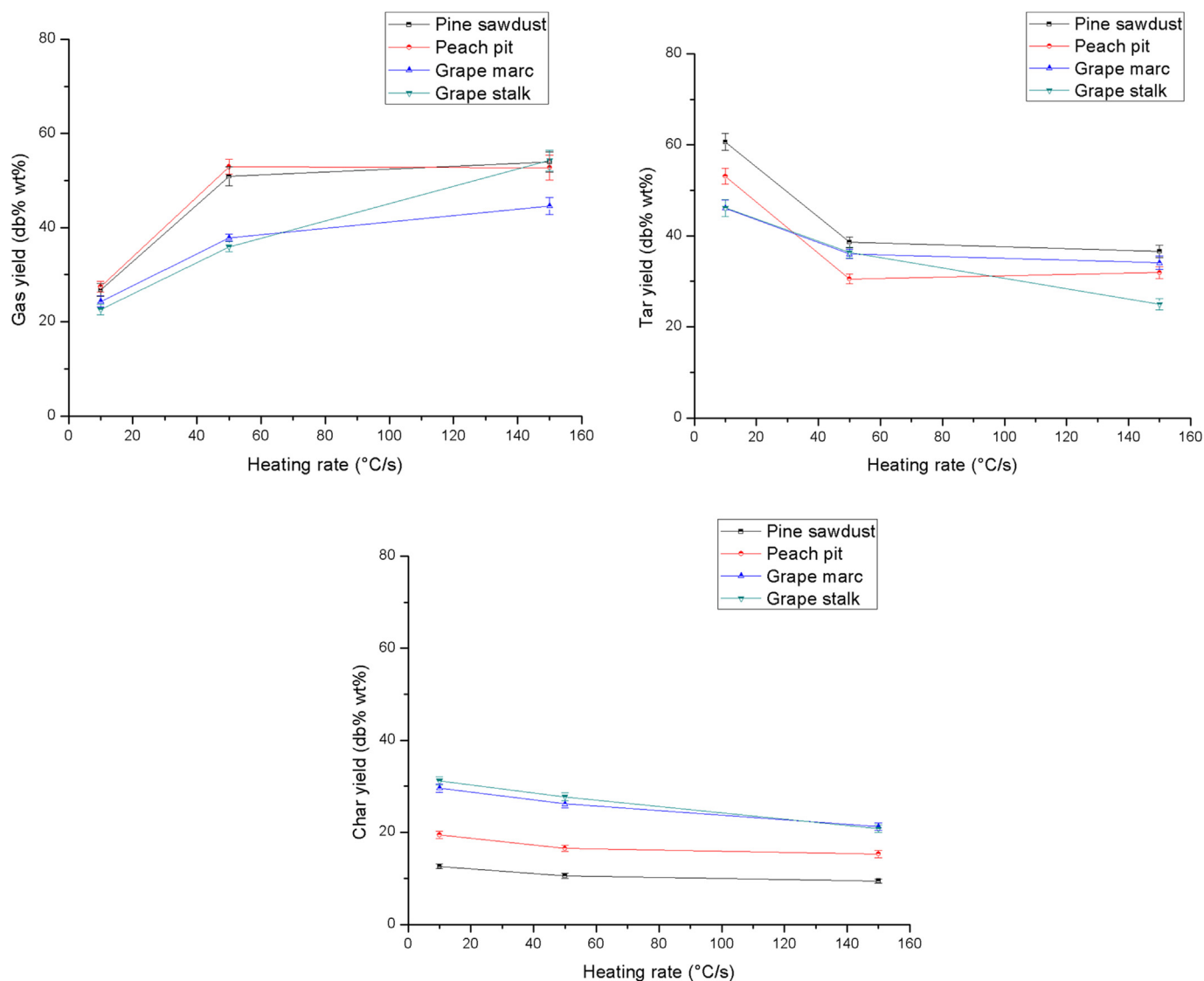


Fig. 5. Effect of heating rate on products yields from biomass pyrolysis at final temperature 1200 °C.

3. Results and discussion

3.1. Effect of final temperature

Fig. 2 presents the distribution of pyrolysis products (Fig. 2 a: gas yield; Fig. 2b; tar yield; Fig. 2c: char yield, respectively) as a function of the final temperature (range: 800–2000 °C), with heating rate of 50 °C/s, for the 4 types of biomass. At 50 °C/s heating rate, the higher the final pyrolysis temperature, the higher the gas yield and the lower the tar and char yields. For all types of biomass, the temperature influence is strong between 800 °C and 1200 °C for the gas and tar yields, then it levels. The decrease tendency is weaker for the tar yield. At 2000 °C, the biomass composition has little to no influence on the product distribution. As shown in Fig. 2a, the gas yields of pine sawdust and peach pit increase from 29.4% to 55.4% between 800 °C and 1200 °C then they slightly increase to 55.4% at 1600 °C. The highest gas yield of 63.5% is obtained from pine sawdust at final temperature 2000 °C, and gas yields for other biomass samples are less than 10% lower only.

Fig. 2b points out that, at 50 °C/s heating rate, the biomass composition has very little influence on the tar yield as soon as the

biomass sample is pyrolyzed at temperature higher than 1200 °C, and this influence is negligible above 1600 °C. The increase in gas yield with temperature is due to the secondary tar cracking [28]. A high final temperature favors the tar secondary reactions into gas in the biomass pellet. Besides, a hot zone near the sample surface and considerable tar secondary reactions may occur. Numerous researches have studied the effect of temperature on the product yields [29–33]. At temperatures such as those considered in this study (>800 °C), the product distribution greatly depends on the tar secondary reactions. Tar secondary reactions are classified as homogeneous and heterogeneous, and they include such processes as cracking, partial oxidation, (re)polymerization ... Condensation may also happen [34]. These secondary reactions result in an extra tar decomposition and syngas formation. The pyrolysis reaction scheme is presented in Fig. 3 [35], fast pyrolysis proceeds through the primary and secondary reactions. The pellet increases intra-particle residence times of vapors. The high temperatures favor the gas production by enhancing secondary reactions [35]. This explains why the gas yields increase with the final temperature whereas the tar and char yields present opposite trends.

The effect of the final temperature on the gas compositions

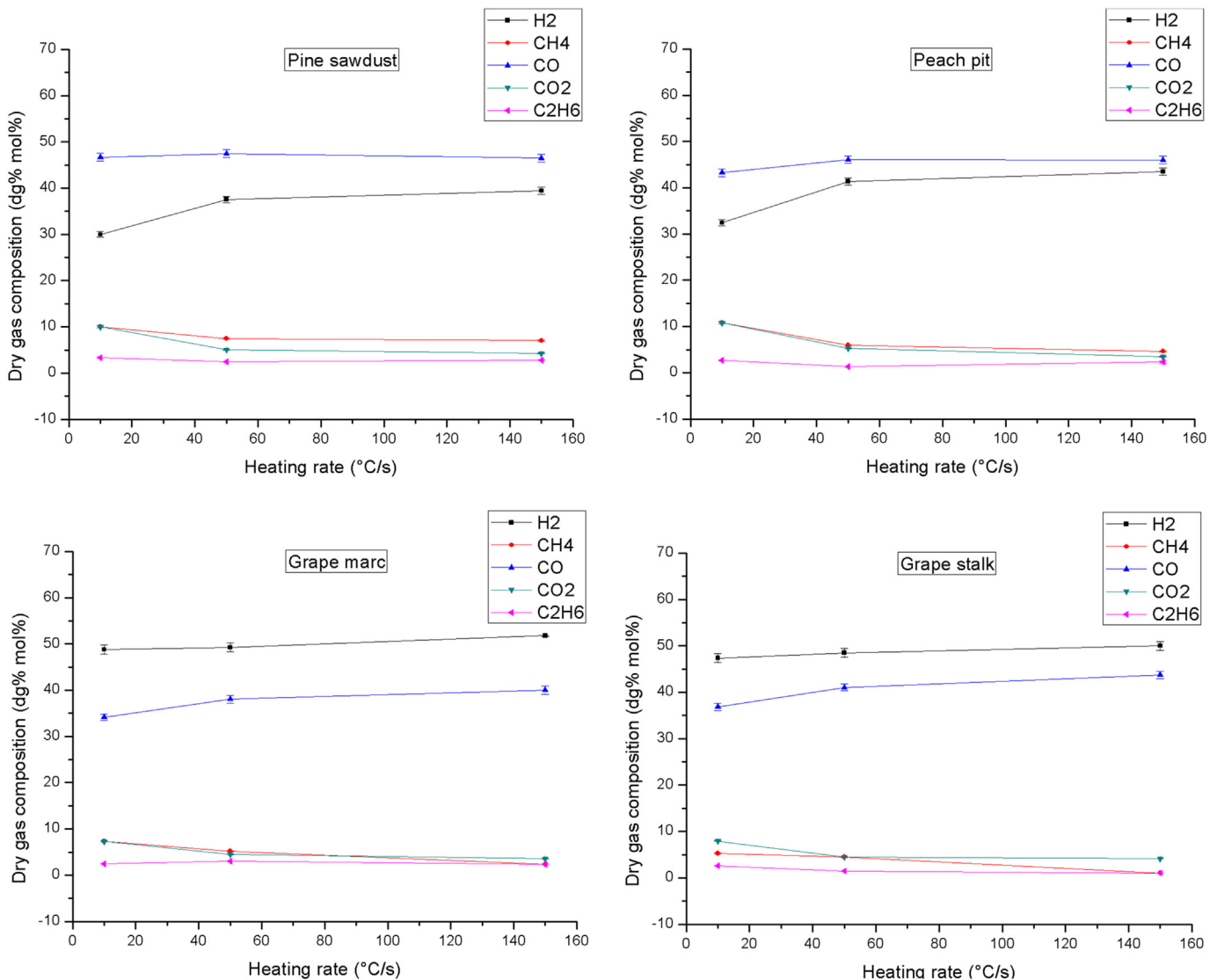


Fig. 6. Effect of heating rate on dry gas composition from biomass pyrolysis at final temperature 1200 °C.

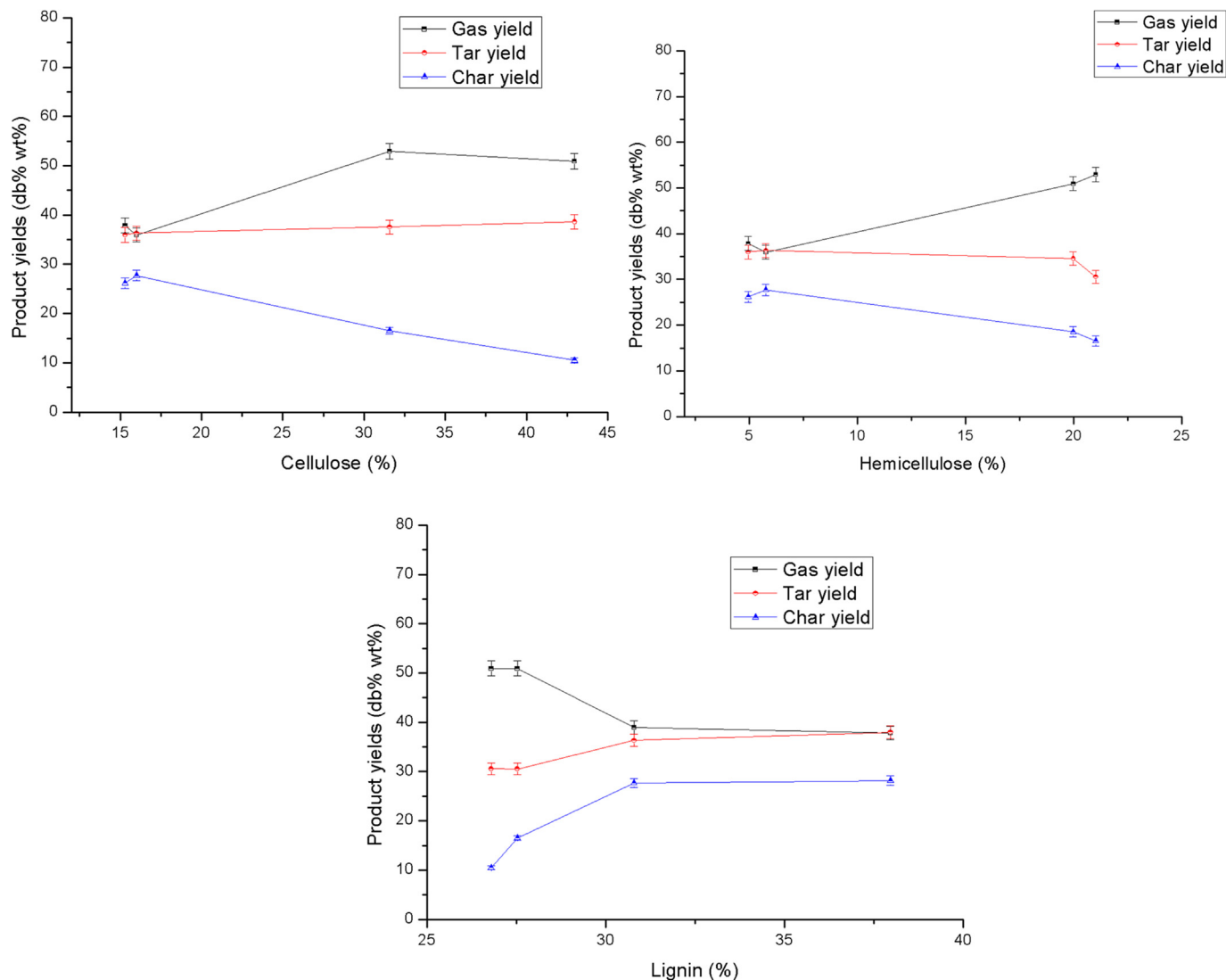


Fig. 7. Effect of lignocelluloses on product yields from biomass pyrolysis at final temperature 1200 °C and heating rate of 50 °C/s.

issued from pyrolysis of the 4 types of biomass at the heating rate of 50 °C/s is presented in Fig. 4 (Fig. 4a: pine sawdust; Fig. 4b: peach pit; Fig. 4c: grape marc; Fig. 4d: grape stalk, respectively). Whatever the biomass, CH₄, C₂H₆ and CO₂ contents decrease noticeably when the pyrolysis final temperature increases from 800 up to 1200 °C, then the inclination is the same but the influence is weak. In all cases, the CO₂ plots confirm the occurrence of secondary reactions in gas phase. And CH₄ and C₂H₆ contents decrease with temperature, since these molecules are not stable at temperature higher than 800 °C and they are more and more cracked [36]. For pine sawdust and peach pit, H₂ content increases deeply with temperature and CO content is almost not affected, as shown in Fig. 4a and b. Oppositely, Fig. 4c and d shows that CO contents increase with the final temperature for grape marc and grape stalk, while H₂ contents is not affected by the temperature. Finally, these two biomass groups differ also strongly with respect to the H₂/CO ratio. For grape marc and grape stalk it is always larger than 1 (1.3 and 1.2 at 1200 °C respectively) but this ratio is always less than 1 for pine sawdust (almost equal to one at 1600 °C only) and it changes at about 1400 °C for peach pit, less than one under 1400 °C and almost equal to one above 1400 °C. These opposite trends of the gaseous production (CO and H₂) of biomass solar pyrolysis are

mainly due to the different lignocellulose contents (in particular cellulose) of the considered types of biomass, as explained later in the paper.

3.2. Effect of heating rate

The biomass sample heating rate is another important parameter of biomass solar pyrolysis. It indicates the ability to heat the biomass particles in the hot zone. The heating rate also influences the residence time of the volatiles in the hot zone; as shown earlier, the higher the heating rate, the shorter the residence time [37]. Since the hot zone of this solar pyrolysis reactor is relatively small [8], the first effect induces the products' distribution. As shown in Fig. 5, the gas yields increase with the heating rate (Fig. 5a) while the tar yields decrease (Fig. 5b), whatever the type of biomass. This is due to the enhanced tar and char cracking reactions, caused by the reduction of the heat and mass transfer limitations when the heating rate increases [38]. Once heat and mass transfer limitations are overcome, the liquid and gas yields stabilize with further increase in heating rate [39], and the gas yield variation is not so strong when the heating rate is higher than 50 °C/s. It is also observed in Fig. 5b that a relatively low heating rate can greatly

favor the liquid production of solar pyrolysis. The highest tar yield of 65.3% is obtained with pine sawdust pyrolyzed at final temperature of 800 °C and heating rate of 10 °C/s. As indicated in Fig. 5c, for all biomass samples, the heating rate has very little influence and the char yield decrease with the heating rate is weak. Nevertheless, the reduction of the tar residence time inside the sample with increasing heating rate may explain this decrease [40].

Fig. 6 presents the influence of the heating rate on the product gas composition. The gas composition clearly depends on the type of biomass and again the pine sawdust and peach pit behavior differs from that of grape by-products: whereas the pyrolyzed grape by-products (both grape stalk and grape marc) produce about 50% H₂ and 35–42% CO whatever the heating rate, the pine sawdust and peach pit pyrolysis produces more CO (43–48%) than H₂ (30–40%) this means that the H₂/CO ratio is always greater than 1 for grape by-products but always smaller than 1 for pine sawdust and peach pit. For all kinds of biomass, the CO₂, CH₄ and C₂H₆ production is much lower (0–10%) than that production of H₂ and CO, it slightly decreases with increasing heating rate from 10 °C/s to 50 °C/s, then it remains stable. For all biomass wastes, the most obvious influence of heating rate on the gas composition is between 10 and 50 °C/s. The gas composition remains relatively stable

for higher heating rates. This result is in perfect agreement with previous results concerning the heating rate influence on the product yields.

3.3. Effect of lignocellulose composition

Taking advantage of the various compositions in lignocelluloses of the four types of waste biomass, the effect of lignin and cellulose contents on the pyrolysis product yields at final temperature of 1200 °C and heating rate of 50 °C/s could be studied, and the results are plotted in Fig. 7. It can be seen that the char and tar yields increase with the lignin content, whereas the gas yield decreases. Indeed, lignin pyrolysis produces more char than cellulose and hemicellulose pyrolysis. As shown before in Fig. 2a, and Fig. 2c, both grape by-products, which contain more lignin than peach pit and pine sawdust, present higher char yields and lower gas yields when pyrolyzed. This result is in agreement with Fahmi et al.'s observation [41] on the effect of lignin on liquid yields. Similarly, it was shown that the higher the hemicellulose content, the lower the char and tar yields and the higher the gas yields: hemicellulose pyrolysis produces more volatiles, less char and less tar than cellulose pyrolysis [42].

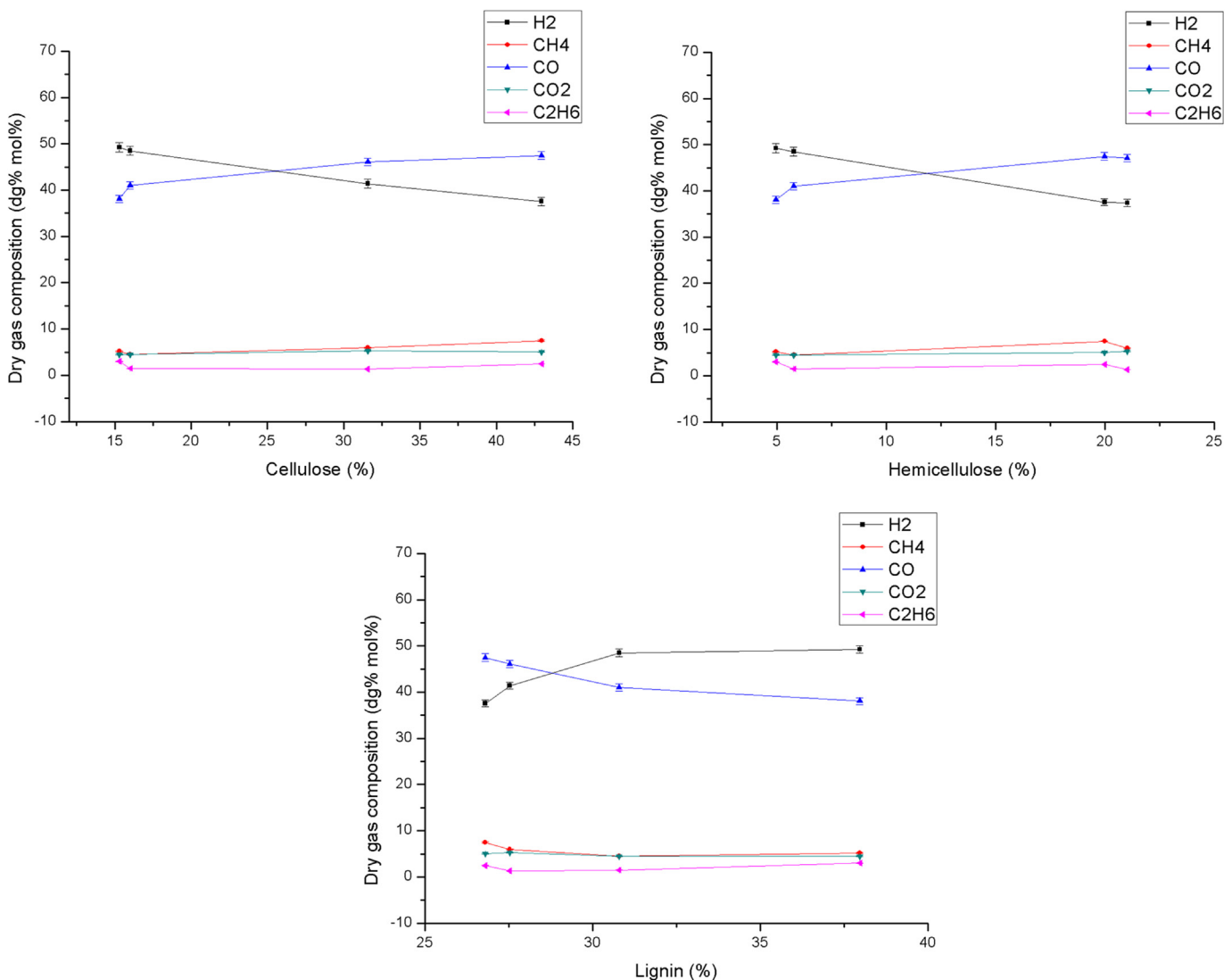


Fig. 8. Effect of lignocelluloses on dry gas composition from biomass pyrolysis at final temperature 1200 °C and heating rate of 50 °C/s.

The effect of the biomass composition (lignocellulose components) on the pyrolysis produced gas composition is presented in Fig. 8. It can be seen that CO production increases with the cellulose and hemicellulose content and it decreases with the lignin content. Oppositely, H₂ production decreases with the cellulose and hemicellulose contents and it increases with the lignin content. As a result, the H₂/CO ratio exceeds unity for the following composition: cellulose content smaller than 25 wt%, hemicellulose content below about 12% and lignin content in excess of 29%. This is mainly due to the lignin pyrolysis that forms more H₂ whereas cellulose and hemicellulose pyrolysis produces more CO and hydrocarbons.

4. Conclusion

Fast pyrolysis of four kinds of agricultural and forestry biomass by-products was conducted in a lab-scale solar reactor to investigate the influences of final temperature, heating rate and lignocellulose composition on the product yields and gas composition.

The pyrolysis experimental results showed that higher final temperature and heating rate favor the syngas production and the tar decomposition. The highest gas yield of 63.5wt% was obtained from pine sawdust at 1200 °C and 50 °C/s. Higher lignin content can enrich the char production, whereas higher cellulose and hemicellulose contents increase the gas yields.

CO₂, CH₄ and C₂H₆ contents decrease with the pyrolysis final temperature. The CO content of the pyrolysis gas increases with the cellulose and hemicellulose contents, whereas the H₂ content increases with the lignin content. The H₂/CO ratio is always greater than one for both grape by-products, grape marc and grape stalk.

Acknowledgments

This study was conducted in the frame of the SYNOLGAS Project developed in the frame of the Argentinean-French CAFCI collaboration (CNRS-CONICET-MINCYT). It was also supported by French "Investments for the future" programme managed by the National Agency for Research under contract ANR-10-LABX-22-01.

References

- [1] C. Di Blasi, Modeling and simulation of combustion processes of charring and non-charring solid fuels, *Prog. Energy Combust. Sci.* 19 (1993) 71–104.
- [2] M. Van de Velden, J. Baeyens, A. Brems, B. Janssens, R. Dewil, Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction, *Renew. Energy* 35 (2010) 232–242.
- [3] K. Zeng, D.P. Minh, D. Gauthier, E. Weiss-Hortala, A. Nzihou, G. Flamant, The effect of temperature and heating rate on char properties obtained from solar pyrolysis of beech wood, *Bioresour. Technol.* 182 (2015) 114–119.
- [4] A. Nzihou, G. Flamant, B. Stanmore, Synthetic fuels from biomass using concentrated solar energy – A review, *Energy* 42 (2012) 121–131.
- [5] O. Authier, M. Ferrer, G. Mauviel, A.-E. Khalifi, J. Lédé, Wood fast pyrolysis: comparison of Lagrangian and Eulerian modeling approaches with experimental measurements, *Ind. Eng. Chem. Res.* 48 (2009) 4796–4809.
- [6] M.W. Hopkins, C. Dejenga, M.J. Antal, The flash pyrolysis of cellulose materials using concentrated visible light, *Sol. Energy* 32 (1984) 547–551.
- [7] J. Zeaiter, M.N. Ahmad, D. Rooney, B. Samneh, E. Shammas, Design of an automated solar concentrator for the pyrolysis of scrap rubber, *Energy Convers. Manage* 101 (2015) 118–125.
- [8] K. Zeng, D. Gauthier, R. Li, G. Flamant, Solar pyrolysis of beech wood: effects of pyrolysis parameters on the product composition, *Energy* (2015). <http://dx.doi.org/10.1016/j.energy.2015.10.008>.
- [9] K. Zeng, D. Gauthier, J. Lu, G. Flamant, Parametric study and process optimization for solar pyrolysis of beech wood, *Energy Convers. Manage* (2015). <http://dx.doi.org/10.1016/j.enconman.2015.10.039>.
- [10] M. Van de Velden, J. Baeyens, I. Boukis, Modeling CFB biomass pyrolysis reactors, *Biomass Bioenergy* 32 (2) (2008) 128–139.
- [11] A.V. Bridgwater, G.V.C. Peacocke, Fast pyrolysis processes for biomass, *Renew. Sustain. Energy Rev.* 4 (2000) 1–73.
- [12] Hugh N. Stiles, Rafael Kandiyoti, Secondary reactions of flash pyrolysis tars measured in a fluidized bed pyrolysis reactor with some novel design features, *Fuel* 68 (3) (2003) 275–282.
- [13] A.M. Li, X.D. Li, S.Q. Li, Y. Ren, Y. Chi, J.H. Yan, K.F. Cen, Pyrolysis of solid waste in a rotary kiln: influence of final pyrolysis temperature on the pyrolysis products, *J. Anal. Appl. Pyrolysis* 50 (2) (1999) 149–162.
- [14] R. Zanzi, K. Sjöström, E. Björnbom, Rapid high-temperature pyrolysis of biomass in a free-fall reactor, *Fuel* 75 (5) (1999) 545–550.
- [15] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass Bioenergy* 38 (2012) 68–94.
- [16] K. Maniatis, J. Baeyens, H. Peeters, G. Roggeman, The EGEMIN Flash Pyrolysis Process: Commissioning and Initial Results. *Advances in Thermochemical Biomass Conversion*, Springer, Netherlands, 1993, pp. 1257–1264.
- [17] D. Neves, H. Thunman, A. Matos, L. Tarelho, A. Gómez-Barea, Characterization and prediction of biomass pyrolysis products, *Prog. Energy Combust. Sci.* 37 (2011) 611–630.
- [18] J. Akhtar, N.S. Amin, A review on operating parameters for optimum liquid, *Renew. Sustain. Energy Rev.* 16 (2012) 5101–5109.
- [19] M. Balat, M. Balat, E. Kirtay, H. Balat, Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: pyrolysis systems, *Energy Convers. Manage* 50 (2009) 3147–3157.
- [20] E. Pütün, Catalytic pyrolysis of biomass: effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst, *Energy* 35 (2010) 2761–2766.
- [21] J. Akhtar, N.S. Amin, A review on operating parameters for optimum liquid, *Renew. Sustain. Energy Rev.* 16 (2012) 5101–5109.
- [22] E. Salehi, J. Abedi, T. Harding, Bio-oil from Sawdust: pyrolysis of sawdust in a fixed-bed system, *Energy Fuel* 23 (2009) 3767–3772.
- [23] P.T. Williams, S. Besler, The influence of temperature and heating rate on the slow pyrolysis of biomass, *Renew. Energy* 7 (1996) 233–250.
- [24] J. Akhtar, N.S. Amin, A review on operating parameters for optimum liquid, *Renew. Sustain. Energy Rev.* 16 (2012) 5101–5109.
- [25] S. Mahmoudi, J. Baeyens, J. Seville, NO_x formation and selective non-catalytic reduction (SNCR) in a fluidized bed combustor of biomass, *Biomass Bioenergy* 34 (9) (2010) 1393–1409.
- [26] H.P. Yang, R. Yan, H.P. Chen, D.H. Lee, C.G. Zheng, Characteristics of hemicelluloses, cellulose and lignin pyrolysis, *Fuel* 86 (2007) 1781–1788.
- [27] F. Abnisa, W. Daud, A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil, *Energy Convers. Manage* 87 (2014) 71–85.
- [28] O. Onay, Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well-swept fixed-bed reactor, *Fuel Process Technol.* 88 (2007) 523–531.
- [29] P. Williams, S. Besler, The influence of temperature and heating rate on the slow pyrolysis of biomass, *Renew. Energy* 7 (3) (1996) 233–250.
- [30] P. Horne, P. Williams, Influence of temperature on the products from the flash pyrolysis of biomass, *Fuel* 75 (9) (1996) 1051–1059.
- [31] A. Demirbas, Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues, *J. Anal. Appl. Pyrolysis* 72 (2) (2004) 243–248.
- [32] M. Garcia-Perez, X.S. Wang, J. Shen, M.J. Rhodes, F. Tian, W.-J. Lee, et al., Fast pyrolysis of oil mallee woody biomass: effect of temperature on the yield and quality of products, *Industrial Eng. Chem. Res.* 47 (2008) 1846–1854.
- [33] A.E. Pütün, N. Özbay, E. Apaydin Varol, B.B. Uzun, F. Ates, Rapid and slow pyrolysis of pistachio shell: effect of pyrolysis conditions on the product yields and characterization of the liquid product, *Int. J. Energy Res.* 31 (2007) 506–514.
- [34] P. Morf, P. Hasler, T. Nussbaumer, Mechanisms and kinetics of homogeneous secondary reactions from continuous pyrolysis of wood chips, *Fuel* 81 (2002) 843–853.
- [35] A.V. Bridgwater, *Fast Pyrolysis of Biomass: a Handbook*, 3, CPL Press, Newbury (UK), 2005, pp. 121–146.
- [36] M. Khan, B. Crynes, Survey of recent methane pyrolysis literature, *Indus. Eng. Chem.* 62 (10) (1970) 54–59.
- [37] J. Gibbins-Mathame, R. Kandiyoti, Coal pyrolysis yields from fast and slow heating in a wire-mesh apparatus with a gas sweep, *Energy Fuels* 2 (1988) 505–511.
- [38] E. Salehi, J. Abedi, T. Harding, Bio-oil from Sawdust: pyrolysis of sawdust in a fixed-bed system, *Energy Fuel* 23 (2009) 3767–3772.
- [39] J. Akhtar, N.S. Amin, A review on operating parameters for optimum liquid, *Renew. Sustain. Energy Rev.* 16 (2012) 5101–5109.
- [40] Y. Chhiti, S. Salvador, J.-M. Commandré, F. Broust, Thermal decomposition of bio-oil: Focus on the products yields under different pyrolysis conditions, *Fuel* 102 (2012) 274–281.
- [41] R. Fahmi, A. Bridgwater, I. Donnison, N. Yates, J.M. Jones, *Fuel* 87 (2008) 1230–1240.
- [42] E.J. Soltes, T.J. Elder, *Pyrolysis*, in: I.S. Goldstein (Ed.), *Organic Chemicals from Biomass*, 63–95, CRC Press Inc., Boca Raton, FL, 1981.