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Ex situ thermo-catalytic upgrading of biomass pyrolysis vapors using a traveling wave microwave reactor

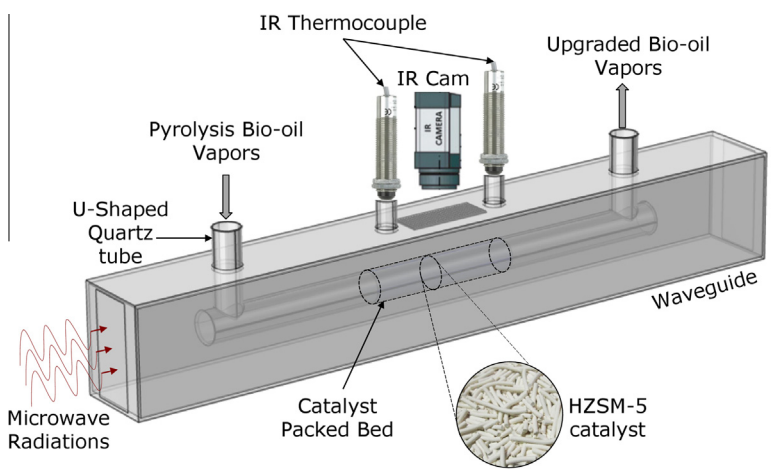
P.D. Muley [a], C.E. Henkel [b], G. Aguilar [b], K.T. Klasson [c], D. Boldor [b,*]

[a] Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, United States
[b] Department of Biological and Agricultural Engineering, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, United States
[c] United States Department of Agriculture, Agricultural Research Service, New Orleans, LA 70214, United States

HIGHLIGHTS

- *Ex-situ* microwave reactor was used to heat catalyst bed for pyrolysis upgrading.
- Results were compared with conventional catalytic reactor.
- Microwave heating yielded higher aromatic compounds.
- Catalyst deactivation due to coking was lower in microwave reactor.
- 30% decrease in energy input for microwave reactor.

GRAPHICAL ABSTRACT



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ABSTRACT

Microwave heating offers a number of advantages over conventional heating methods, such as, rapid and volumetric heating, precise temperature control, energy efficiency and lower temperature gradient. In this article we demonstrate the use of 2450 MHz microwave traveling wave reactor to heat the catalyst bed for thermo-catalytic upgrading of pyrolysis vapors. HZSM-5 catalyst was tested at three different temperatures (290°, 330° and 370 °C) at a catalyst to biomass ratio of 2. Results were compared with conventional heating and induction heating method of catalyst bed. The yields of aromatic compounds and coke deposition were dependent on temperature and method of heating. Microwave heating yielded higher aromatic compounds and lower coke deposition. Microwave heating was also energy efficient compared to conventional reactors. The rate of catalyst deterioration was lower for catalyst heated in microwave system.
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1. Introduction

Pyrolytic bio-oil is a complex mixture of different sized organic molecules such as phenols, furans, levoglucosan, and other compounds, [1,2] formed as a result of the depolymerization and

* Corresponding author at: 149 EB Doran Building, Department of Biological and Agricultural Engineering, LSU AgCenter, Baton Rouge, LA 70803, United States.
E-mail address: DBoldor@agcenter.lsu.edu (D. Boldor).

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fragmentation of the biomass feedstock components (cellulose, hemicellulose, and lignin) during pyrolysis. Although bio-oil produced from fast pyrolysis of biomass has a potential to be directly used as a liquid fuel, this fuel has certain limitations such as high viscosity, acidity, low heating value, high ash content, etc. [3]. Pyrolytic bio-oil also has high oxygen content of about 40% which marks a major difference between pyrolysis fuel and hydrocarbon fuel (oxygen content < 1%) [3]. High oxygen content leads to a decrease in energy density [1] and catalytic deoxygenation of bio-oil is the most effective way to reduce oxygen content [4,5]. In this process, pyrolysis vapors are upgraded with the catalyst; where deoxygenation and cracking reactions takes place, and oxygen is released in the form of water, CO_2, and CO.

Numerous studies have been performed over the years to study the effect of various catalysts on pyrolysis vapor upgrading, with most of them using the 300° to 500 °C as the operating temperature range [1,6–11]. Zeolites such as HZSM-5 have proved to be one of the most effective catalyst for deoxygenation of bio-oil when operating in the temperature range of 250–400 °C [7]. The major disadvantages of catalytic upgrading of pyrolysis bio-oil are heat loss by heat transfer medium such as sand, non-uniform heating of catalyst in externally heated reactors and the issues associated with the deactivation of catalytic sites via either coke deposition or poisoning [1,12]. In spite of smart heat transfer designs, conventional heating technologies lack a rationally designed method for efficient and optimum use of imparted energy to achieve a desired temperature distribution.

Use of electromagnetic energy in the microwave region (300–6000 MHz) is an effective heating mechanism as microwaves impart energy directly to the material and eliminates the need of a heat transfer medium [13]. These qualities of microwave heating make it an efficient heating method, with a conversion efficiency of electrical energy to heat of 80–85% [14]. Apart from increased heating efficiency, microwave heating of catalyst may improve catalyst performance compared to conventional heating, mainly due to an increase in rate of reaction as described by Arrhenius equation [15]

$$K = Ae^{\frac{-Ea}{RT}} \quad (1)$$

where K – Rate constant, Ea – Activation energy (J mol^{-1}), R – Gas constant (J K^{-1} mol^{-1}), T – Temperature (K), A – pre-exponential factor.

The frequency factor A represents molecular mobility and depends on the frequency of vibration of reacting molecules at the reaction interface which is directly affected by the microwave irradiation. An increase in frequency factor indicates increased rate of collision, thus, increases the rate of reaction [15]. Moreover, microwave heating of catalyst is known to reduce coke deposition on the surface due to self-gasification of coke peculiar to microwave reactions only [16]. Microwave irradiated coke tend to desorb from the surface of the catalyst, and microwave heating is also an effective means of desorption of polar molecules [17]. These advantages of microwave technology make it a viable option for catalyst heating.

Microwave heating has been previously studied for pyrolysis of biomass as well as catalytic upgrading [18–20]. However, all the studies reported were *in situ* catalytic upgrading. *In-situ* catalytic upgrading puts limitations on the pyrolysis temperature as most catalysts are efficient at 200–500 °C [7], while pyrolysis is most efficient above 500 °C for maximum liquid yields. Moreover, *ex situ* catalytic upgrading has shown to increase both yield and deoxygenation rate compared to *in situ* upgrading [21,22]. The objective of this study was to develop an *ex-situ* microwave-assisted catalytic upgrading process for pyrolysis vapors that will help promote the understanding of fundamental catalytic requirements for deoxygenation of pyrolysis vapors and the role of microwaves in catalyst activity and heating efficiency.

Pyrolysis of biomass was performed in an induction heater and the exiting bio-oil vapors were passed over a hot catalyst bed heated using a traveling wave microwave reactor. The performance of the microwave process was compared to conventionally and inductively heated catalyst bed processes in terms of yield and quality of the produced bio-oil, as well as with respect to catalyst performance. The conversion of biomass using the proposed method can lead to significant improvements in energy production from renewable resources in terms of increased energy efficiency and biofuel quality, as well as toward developing sustainable energy systems.

2. Materials and methods

2.1. Material

Pine sawdust was obtained from scrap wood at Biological and Agricultural Engineering wood shop at the Louisiana State University Agricultural Center. The sawdust was finely ground and its moisture content was measured. Nitrogen gas cylinder was supplied by Air Liquide (Houston, TX, USA). The HZSM-5 catalyst was supplied by Sigma Aldrich (St. Louis, MO, USA). The biomass pyrolysis reactor was a 5 kW RDO induction heater operating at a frequency range of 35–100 kHz (RDO Induction LLC, Washington, NJ). The reaction tube was a 310-stainless steel tri-clamp tube, 419 mm in length with an inner diameter of 34.4 mm. Reaction tube temperature was controlled using a calibrated Omega IR2C series infrared feedback controller (Omega, Stamford, CT) and an IR sensor to monitor the temperature.

For upgrading reaction, the catalyst was heated by three different methods;

1. Conventional heating using a 13 mm × 1220 mm high temperature heavy insulated heating tape with 313 W output operating at 120 V (Briskheat Corporation, Columbus OH, USA) surrounding the reaction tube. The temperature was measured using a K type thermocouple and controlled using a bench top temperature controller from Briskheat Corporation (Columbus, OH).
2. Induction heating using a 5 kW RDO induction heater operating at frequency range of 135–400 kHz (RDO Induction LLC, Washington, NJ) to heat the catalyst bed. The reaction tube temperature was controlled using a calibrated Raytek MI3 series infrared remote temperature sensor (Raytek Corporation 1999–2014) that was coupled with a PID controller (Red Lion P-1641100, Red Lion Controls Inc. York, PA, USA). For both conventional and induction heating methods, the reaction tube was a 310-stainless steel tri-clamp tube, which was 270 mm length with inner diameter of 25.4 mm [23].
3. Microwave heating using a 1.2 kW, 2450 MHz microwave system. A 2450 MHz microwave traveling wave applicator was modified to accommodate the catalytic bed. The reaction tube was fabricated from quartz with 28.0 mm inner diameter and 472.7 mm in length. The tube was designed to meet the microwave waveguide safety requirement, where a hole in the waveguide is less than 1/3 of the wavelength. The length of the tube was selected such that two IR pyro sensors measured the catalyst temperature at two different points and a thermal camera measured the temperature of the catalyst through a metallic mesh region of the waveguide.

In addition to the microwave safety criteria described above, the dimensions and configuration of the tube were selected considering the ease of loading and unloading of the catalyst and cleaning the tube. Catalyst bed temperature was controlled by using a PID

controller (Red Lion P-1641100, Red Lion Controls Inc. York, PA, USA) which adjusted the anode current of the microwave generator depending on the desired set temperature. The controlled variable was the temperature from the IR sensor fitted over the waveguide, focused on the catalyst bed. The emissivity and transmittance values of the tube were measured and accounted for in the calibration of the non-contact IR sensor (Raytek M13, Raytek Corporation, Wilmington, NC). The temperature was continuously cross-verified using two other temperature sensors (Omega OS137 series, Omega Engineering, Stamford, CT) and a thermal camera (FLIR A40, FLIR Systems, Wilsonville, OR) focused on the catalyst bed.

2.2. Procedure

Microwave upgrading experiments were performed and results were compared with induction and conventional upgrading methods as different heating mechanisms (initial pyrolysis was performed in a separate induction pyrolysis reactor). Thirty grams of finely ground sawdust was placed in the pyrolysis reactor and decomposed at 600 °C according to our previously reported studies [23,24]. The system was purged of Oxygen using Nitrogen gas at 1 L/m for 20 min. The vapors obtained from the pyrolysis reactor were passed over heated HZSM-5 catalyst . Quantitative and qualitative analysis of bio-oil and catalyst was performed and contrasted with results from inductively heated and conventionally heated catalyzed reactions. All upgrading experiments were carried out at three different temperatures (290, 330 and 370 °C). These temperatures were chosen based on our previous study using HZSM-5 as catalyst [23]. Data was statistically analyzed at 95% confidence interval ($\alpha = 0.05$) by performing parametric mean comparisons between different temperatures and heating methods. P-value or calculated probability <0.05 signifies that at least two treatments are significantly different at 95% confidence interval.

Based on the results obtained from our earlier studies [23] for different catalyst to biomass ratios (1:1, 1:1.5 and 1:2), 1:2 C/B ratio was most effective in terms of high aromatics yield, hence, this ratio was chosen to study the effect of different heating mechanisms and temperatures. The same catalyst was used twice for each ratio and temperature combination as two separate experiments to study the extent of deactivation and coke deposition of catalyst in repeat conditions. A heating tape was used to maintain the gas line temperature above 275 °C between the pyrolyzer and the catalytic reactor, so as to avoid inline condensation and minimize secondary reactions. All experiments were performed in duplicates for reproducibility. The detailed bio-oil collection system is given elsewhere [24]. In brief, it consists of an electrostatic precipitator (ESP) that was built in house and a 500 mL flask suspended in an ice bath where the resulting upgraded vapors were condensed (Fig. 1).

The incondensable gases were passed through an ethanol and water trap before being vented with samples being collected in gas sample bags. The system was allowed to cool down for 40–50 min. Liquid was drained in a glass vial, weighed and stored at −20 °C to avoid further polymerization reactions during storage. The char and catalyst were also collected, weighed and stored.

2.2.1. Product characterization

Liquid, gas and char yields were quantified. Yields were calculated based on initial biomass weight. The gas yield was determined by difference based on liquid and char yield. Water content of liquid samples was determined using Karl-Fischer titration as described in literature [25]. Composition of liquid samples was determined via GCMS (Varian 1200 series, Agilent Technologies, Santa Clara, CA) for product identification. Bio-oil samples were also analyzed using a GC-FID using a 30 m HP-5 capillary column. The GC-FID oven was programmed from 40 °C, hold time 6 min, and ramped at 4 °C/min to 250 °C with a holding time of 10 min. Quantification of compounds on the GC-FID was obtained by external standard method. Elemental analysis of oil, char and catalyst samples was conducted using Perkin-Elmer 2400 (PerkinElmer Inc. Waltham, MA) elemental analyzer as previously described [25]. High heating values of the liquid samples were measured using bomb calorimeter (Parr Instrument Company, Moline, IL.) according to the procedure described in literature [26].

2.2.2. Catalyst characterization

Catalyst surface was characterized using different techniques to investigate the extent of coking and deactivation. X-ray photoelectron spectroscopy (XPS) was used to identify and quantify the different elements present in the catalyst using a Kratos Axis 165 X–ray photon spectroscope/auger electron spectroscope operated with Mono-Al Ka X-ray source with beam current at 10 mA and HT at 12 kV (Kratos Analytical Ltd. Manchester, UK). Catalyst surface area and pore volumes were measured using standard BET surface analysis method using N_2 gas adsorption isotherms at −196 °C with a cross sectional area of N_2 molecule as 0.162 nm^2. The catalyst samples were degassed overnight at 350 °C under

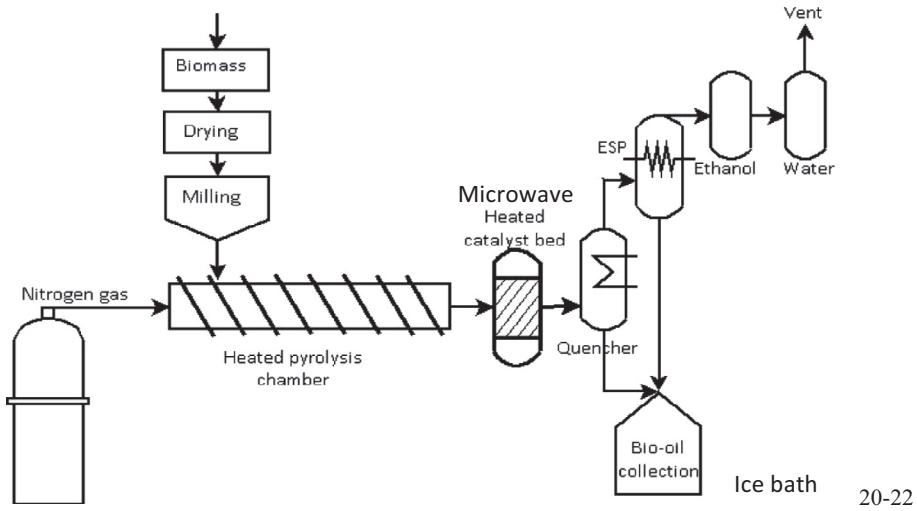


Fig. 1. Flowchart for upgrading of pyrolysis vapors in a microwave heater.

vacuum prior to analysis. The analysis was performed using a NOVA 2200e series Surface area and Pore Size (Quantachrome Instruments Inc., Boynton Beach, FL). Temperature-programmed desorption of ammonia (NH3-TPD) analysis was carried out using Micrometritics 2700 chemisorption apparatus (Micromeritrics Corporation, Norcross, GA). Briefly, 0.05 g of prepared sample was loaded in the U-tube, the sample was degasses using He gas at 500 °C for 30 min. The sample was then cooled to 100 °C and ammonia was adsorbed at the flowrate of 5 °C/min from 100 °C to 500 °C. TCD signal was recorded [27]. The coke deposition on catalyst was determined using elemental analyzer CHN (Perkin Elmer series 2400, Waltham, MA) as previously described [28]. X-ray diffraction (XRD) was used to determine the presence of internal coke in the catalyst, using an Empyrean X-ray Diffractometer (PANalytical, Westborough, MA) [29].

3. Results and discussion

3.1. Pyrolysis yield and product composition

3.1.1. Effect of catalyst bed temperature

Water, bio-oil, gas and char yields were quantified based on initial biomass weight. Char yield for all experiments ranged between 19.87 and 26.97% (Tables 1–3). Since the pyrolysis temperature for all experiments was 600 °C, char yield was not affected by catalyst bed temperature. Elemental analysis (CHNO) of all char samples indicated a composition of 85–88% carbon, 3–6% hydrogen and with traces of nitrogen and sulfur based on total char yield (with the difference as Oxygen). Char was rich in carbon compared to initial biomass samples, which had 46% carbon, 6.43% hydrogen and traces of nitrogen (with the oxygen as difference). Pyrolysis and catalyst bed temperatures play an important role in the quality and quantity of oil [30]. Gas yield was calculated from the difference in biomass input and the liquid and char yield. Gas yield increased as the catalyst bed temperature increased but only marginally; higher catalyst bed temperatures increased the cracking reaction rate which encouraged the formation of non-condensable gases.

Liquid yield is lower for the catalytic upgrading process compared to the non-upgraded products. Liquid yield also slightly decreased as the catalyst bed temperature increased. Total liquid yield was compared to *in-situ* microwave upgrading results reported in literature [20,31,32]. While the temperature and catalyst types were different for *in-situ* upgrading, liquid yield was found to be comparable for both upgrading techniques and varied in the range of 25–35%. Elemental analysis was used to quantify the composition of C, H, N and O in the liquid samples. During catalytic cracking oxygen is removed in the form of water, CO and CO_2 thus reducing the oxygen content of upgraded bio-oil by approximately half compared to non-upgraded bio-oil. Low oxygen and higher carbon content was observed as the catalyst bed temperature increased (p-value < 0.05) (Tables 1–3).

Gas samples were analyzed for composition on a N_2 free basis and were found to be rich in carbon monoxide (20–23 wt%) and carbon dioxide (9–10 wt%) with lower yield of methane (4–6 wt %) and other C_2-C_5 gases (1–3 wt%). About 20–30 wt% of gas composition that was unidentified due to laboratory limitations could mainly comprise hydrogen [33], which contribute to the higher heating values.

3.1.1.1. Water content. Catalytic upgrading removes oxygen in the form of H_2O, CO and CO_2 which is why water content of upgraded bio-oil is higher than that of non-upgraded bio-oil [7]. Tables 1–3 record the total percentage of water and bio-oil in the products. In the liquid product alone, the water fraction is higher for upgraded bio-oil (0.565 for microwave heating run 1) compared to non-upgraded bio-oil (0.457). No specific trend was observed between different temperature ranges. Lower water content was observed for 2nd run where the catalyst was reused for both conventional and microwave heating. This could be because the catalyst activity reduces with reuse and less reaction results in lower water yield. The difference in water content of liquid fraction for the different type of catalyst heating methods, namely, conventional heating, induction heating and microwave heating was less than 5% concluding that both liquid yield and water content were not significantly affected by the method of catalyst heating.

3.1.1.2. Product composition. Non-upgraded bio-oil is generally rich in oxygenated hydrocarbons such as phenols, ketones, alcohol and aldehydes and acids with aromatic compounds detected in insignif-

Table 1
Yield values for upgraded products for three heating methods at 290 °C.

Temperature 290 °C	Non-upgraded bio-oil[a] % Composition	Microwave heating % Composition		Induction heating[a] % Composition		Conventional heating[a] % Composition	
		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Char	19.36	24.87	21.07	21.13	21.37	21.33	20.43
Gas*	25.37	39.53	44.77	51.63	41.50	47.20	46.23
Water	25.28	20.12	18.21	17.47	24.21	21.08	20.23
Bio-oil	29.98	15.48	15.95	9.76	12.92	10.37	13.11
Total	100	100	100	100	100	100	100
CHN analysis of liquid fraction							
Carbon	30.37	60.17	61.92	65.8	61.49	62.35	60.33
Hydrogen	5.85	3.12	4.66	2.06	1.57	3.00	3.35
Nitrogen & sulfur	Traces						
Oxygen*	63.71	36.7	33.42	32.13	36.94	34.64	36.32
Total	99.93	99.99	100	99.99	100	99.99	100
Organic liquid fraction composition (wt% of bio-oil)							
Phenols	53.41	15.55	34.95	30.63	33.67	33.93	37.8
Aliphatic HC	–	14.45	1.47	7.96	4.96	1.71	3.68
Aromatic HC	–	34.12	28.56	27.06	25.5	28.08	26.22
Benzene	–	1.16	–	1.32	1.23	4.44	1.41
Methyl benzene	–	7.22	5.80	12.25	11.29	19.49	17.75
Ethyl benzene	–	1.48	2.68	1.98	–	2.25	0.12
Xylene	–	22.77	11.45	6.54	5.66	0.28	4.63
C9-C10	–	1.14	7.44	4.31	6.45	0.94	1.89

* Determined by difference.
[a] Reproduced from [23] for comparison.

Table 2
Yield values for upgraded products for three heating methods at 330 °C.

Temperature 330 °C	Microwave heating		Induction heating[a]		Conventional heating[a]	
	% Composition		% Composition		% Composition	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Char	26.97	22.50	20.17	21.97	20.93	22.7
Gas*	37.57	45.47	42.90	42.60	48.33	44.23
Water	20.76	20.64	21.29	21.36	20.29	17.59
Bio-oil	14.71	11.39	15.65	14.08	10.44	15.48
Total	100	100	100	100	100	100
CHN analysis of liquid fraction						
Carbon	67.11	68.16	66.2	66.71	69.18	62.82
Hydrogen	3.45	6.61	2.88	2.13	3.15	3.65
Nitrogen & sulfur	Traces					
Oxygen*	29.44	25.22	30.92	31.16	27.67	33.52
Total	100	99.99	100	100	100	99.99
Organic liquid fraction composition (wt% of bio-oil)						
Phenols	29.80	22.57	19.70	21.18	26.48	33.47
Aliphatic HC	2.32	1.67	11.59	19.18	1.48	3.25
Aromatic HC	45.47	40.77	45.13	37.03	42.55	32.56
Benzene	0.46	7.15	2.13	2.49	0.93	5.98
Methyl Benzene	31.49	17.44	10.26	15.63	30.80	8.98
Ethyl Benzene	6.94	1.15	9.94	2.02	2.79	0.38
Xylene	12.87	13.58	5.82	2.30	7.03	13.84
C9-C10	0.88	1.19	16.81	16.99	0.99	2.82

* Determined by difference.
[a] Reproduced from [23] for comparison.

Table 3
Yield values for upgraded products for three heating methods at 370 °C.

Temperature 370 °C	Microwave heating		Induction heating[a]		Conventional heating[a]	
	% Composition		% Composition		% Composition	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Char	22.30	20.26	19.87	21.40	22.70	23.57
Gas*	43.03	49.06	50.23	46.47	47.97	50.07
Water	22.43	18.34	20.21	18.41	19.41	15.37
Bio-oil	12.24	12.32	9.69	13.72	9.91	11.00
Total	100	100	100	100	100	100
CHN analysis of liquid fraction						
Carbon	69.02	67.12	69.46	65.4	69.16	68.41
Hydrogen	3.20	7.93	1.93	2.62	2.40	3.93
Oxygen	27.68	24.95	28.6	31.97	28.38	27.66
Nitrogen & sulfur	Traces					
Total	99.90	100	99.99	99.99	99.94	100
Organic liquid fraction composition (wt% of bio-oil)						
Phenols	5.08	6.10	25.03	32.54	5.53	13.46
Aliphatic HC	1.73	0.13	–	3.09	4.44	–
Aromatic HC	69.64	64.67	63.79	48.76	64.76	57.59
Benzene	1.36	1.21	1.72	0.96	2.28	11.28
Methyl benzene	37.10	38.73	41.46	16.74	39.97	31.30
Ethyl benzene	1.08	2.68	4.01	0.02	2.43	0.16
Xylene	25.10	11.88	3.33	–	13.31	8.53
C9-C10	4.75	6.84	12.61	29.96	6.61	5.45

* Determined by difference.
[a] Reproduced from [23] for comparison.

icant amounts [7,25]. Catalytic upgrading significantly affects these groups. Use of catalyst produces higher yield of non-oxygenated hydrocarbons such as aromatic and aliphatic hydrocarbons which can be blended with gasoline. These hydrocarbons are of interest as fuel replacement and additives. Composition of aromatic hydrocarbons increased as the catalyst bed temperature increased. The aromatic hydrocarbon yield increased from 26% to 28% of total bio-oil yield at 290 °C (Table 1) to 55–65% at 370 °C (Table 3). The actual total aromatic hydrocarbon yield based on the initial weight of biomass increased from 2.9% at 290 °C to 8.5% at 370 °C is consistent with the values reported in the literature for the C/B ratio of 2 [32,34]. The yield achieved is lower compared to the ones reported in literature which varied from 24% to 28% [7,34,35] mainly because a lower C/B ratio of 2 was investigated in the present study in contrary to higher catalyst loading of 5, 10 and 20 reported in these studies [34,35]. At all temperatures, the aromatic HC yield decreased when the catalyst was reused in the second run, marking the decrease in catalyst activity either due to coke deposition, active site poisoning, or both. At lower temperatures, yield of phenols was higher followed by aliphatic hydrocarbons. However, as the temperature rose to 370 °C, the composition of these compounds decreased significantly. These results are in agreement with those noted in literature [7]. Compared to *in-situ* microwave upgrading studies [20,31,32], *ex-situ* process delivered higher yields of deoxygenated aromatics compounds which indicate a much better quality of the deoxygenated product.

3.1.2. Effect of heating method

No change in yield with respect to the heating method used for catalyst heating was observed for gas or char (p-value > 0.05). As stated elsewhere in this article, the difference in water content of liquid fraction for the type of catalyst heating methods, namely, conventional heating, microwave heating and induction heating was less than 5% concluding that neither liquid yield nor water content was significantly affected when the method of heating the catalyst was changed. From the elemental analysis of liquid samples, microwave heating had the lowest oxygen content compared to conventional and induction heating at higher temperatures (330 °C and 370 °C) (Tables 2 and 3). While overall higher carbon values were obtained for bio-oil upgraded over fresh catalyst compared to reused catalyst in conventional and induction heating, for the microwave-based process the carbon content slightly increased for the second run, with much higher hydrogen and lower oxygen compared to the other two heating methods (p-value < 0.05). Highest oxygen content of 36% was observed at 290 °C in run 2 with conventional method (Table 1) and lowest oxygen content of 24% was obtained at 370 °C with microwave heating (Table 3). Higher hydrogen content was also observed in all liquid samples after microwave heating compared to other heating methods showing that production of a higher grade fuel in the microwave reactor.

From the perspective of obtained compounds, high yields of non-oxygenates such as aliphatic or aromatic hydrocarbons is desirable for better quality fuel. Aliphatic hydrocarbon yield was no more than 19 wt% for any combination tested and decreased as the catalyst bed temperature increased. Microwave heating yielded highest aromatic hydrocarbon yield at all temperatures with aromatic HC yield consistently higher for both run 1 and run 2 compared to other methods (p-value = 0.99). The lowest reported aromatic HC yield based on initial weight of biomass was 2.6% at 290 °C obtained by induction heating for reused catalyst reported in our previous work [23], whereas, the highest aromatic HC yield of 8.5% was obtained with microwave heating at 370 °C. Aromatic hydrocarbons mainly consisted of benzene, ethyl benzene, methyl benzene, toluene, xylene and C_9-C_{10}; with the highest composition of methyl benzene and xylene. Benzene content was low at all temperatures and heating methods except for induction heating. The low concentration of benzene is probably due to alkylation reaction on acid cites of the catalyst [7]. Toluene and ethyl benzene composition was also found to be negligible. C_9-C_{10} concentration varied for samples and was greater at higher temperatures but did not follow a specific trend for the type of heating method employed.

3.2. Catalyst characterization

3.2.1. X-ray photoelectron spectroscopy (XPS) analysis and elemental analysis

X-ray photoelectron spectroscopy is used to study the quantity of carbonaceous material present on the catalyst surface on of the material. The most distinct peaks observed on the catalyst were aluminum, silicon, carbon, oxygen and traces of nitrogen, sulfur and hydrogen. Chemical formula for HZSM-5 contains all of the above compounds except carbon, sulfur and nitrogen. Fig. 2 shows the variation in the C/Al peak for catalyst sample at different temperatures and heating method. Occurrence of carbon peak is due to coke deposition on the catalyst surface; in this case, a lower value indicates a better performance. At 290 °C, it was observed that the coke formation was reported to be highest for catalyst heated with conventional heating techniques (C/Al = 3.0583) [23] compared to that of induction heating or microwave heating. Coke formation on acid catalysts like that of HZSM-5 during catalytic cracking is strongly governed by polymerization, condensation and hydrogen elimination reactions. These reactions break the long chain polymers and form aromatic compounds [36]. These reactions are highly temperature dependent and favor higher temperatures, which can explain higher coke deposition at higher temperatures in the microwave heating method.

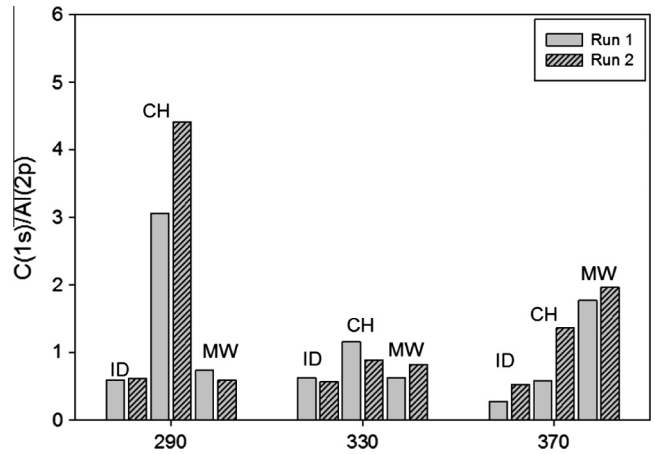


Fig. 2. XPS analysis (C/Al) of catalyst after reaction at different temperatures and heating methods (*CH – conventional heating, *ID – induction heating, MW – microwave heating). *Reproduced from [23].

However, carbon deposition could also occur due to condensation of molecules on cooler catalyst surface. This phenomenon occurs when the catalyst surface is not uniformly heated and cooler spots on the catalyst surface may encourage vapor condensation on the surface and leads to catalyst poisoning and deactivation. Higher coke deposition for lower temperature samples with heating tape (CH – conventional heating) were attributed to this phenomenon [23]. As explained further in the section on surface area, lower coke deposition in microwave could be due by self-gasification of carbon deposited on the catalyst [16].

Since an XPS study is mainly used for surface analysis, even though the samples were finely ground, the results can still be interpreted as surface analysis. Hence we performed elemental analysis of catalyst by combustion to give CHN data that can be considered as bulk analysis (Table S1 in electronic supplementary information (ESI)). The observations made for surface analysis were confirmed by the elemental analysis of catalyst (Fig. 3). High amounts of carbon were obtained at all catalyst temperatures for the conventional heating method. Higher C/H mole ratio suggests that the coke present is aromatic in nature. For microwave upgrading, the C/H mole ratio was observed to increase with temperature (Fig. 3). These results were in agreement with the product composition of bio-oil obtained after upgrading. Nitrogen and sulfur values were negligible for all samples (Table S1).

3.2.2. Surface area analysis

BET surface area and micropore area available after reaction was investigated and compared to fresh catalyst. Total surface area available after reaction directly corresponds to the amount of coke deposited on the catalyst surface. The fresh catalyst surface area as provided by the vendor was 250 m^2/g; our own measurements showed a surface area 247.7 m^2/g (Table 4). More surface area is available for microwave-heated catalyst, followed by induction heating, and lastly by conventionally heated catalyst [23]. Higher surface area after the runs corresponds to lower coke deposition on the catalyst surface. Evidence of self-gasification of coke on catalyst inside a microwave reactor has been established in the past [16]. This self-gasification leads to reaction of coke with CO_2 in the presence of steam to form CO and H_2 gases thus reducing the amount of coke deposited on the catalyst [16]. The reason for self-gasification process might lie in the fact that both catalyst

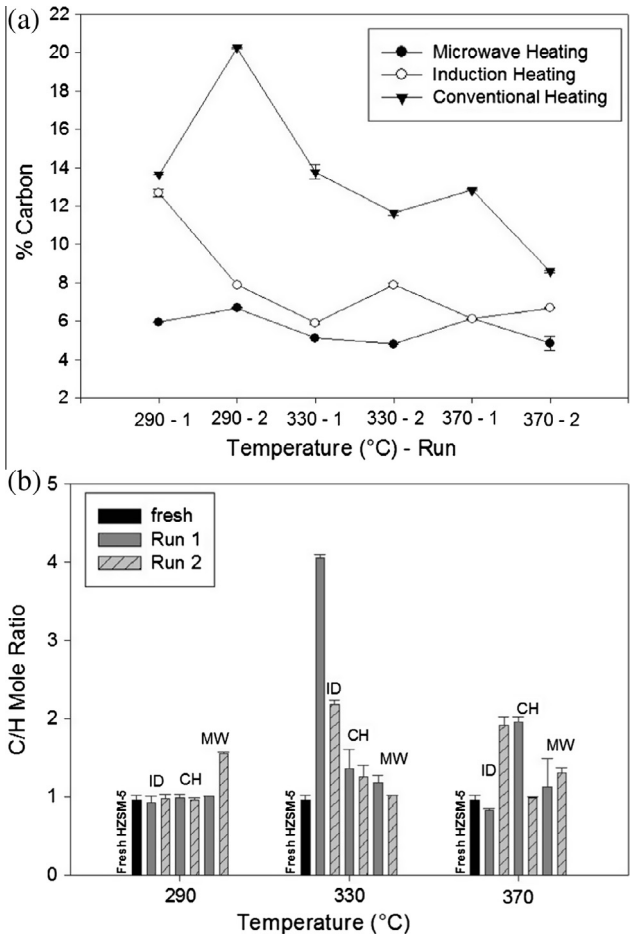
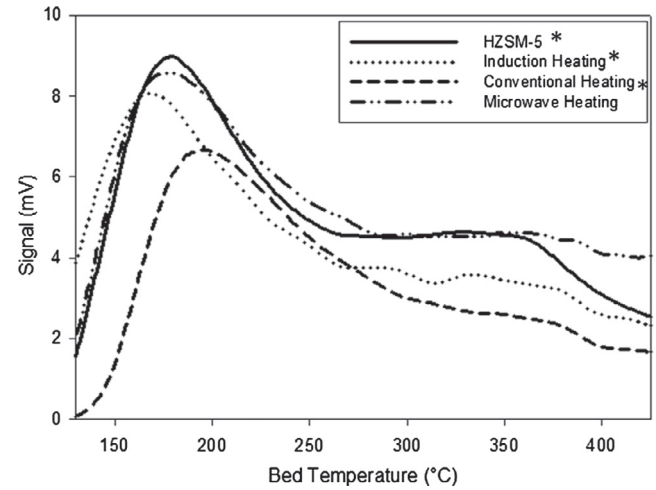


Fig. 3. (a) % Carbon deposition and (b) C/H ratio from elemental analysis (CHNS) for fresh and coked catalyst.

and coke respond to microwave radiations. It is an established fact that coke deposition on zeolite surface is a result of adsorption of coke on catalyst surface [37]. Preliminary tests have showed that microwave desorption is an effective technique for the removal of polar adsorbates compared to conventional heating due to the direct volumetric heating achieved in the microwave reactor [17,38]. In this particular case, both coke (the adsorbate) and the HZSM-5 catalyst (the adsorbent) readily heat in the microwave creating a unique situation where desorption with microwave heating is highly plausible [17]. Another prominent effect that microwaves create is occurrence of micro-plasmas and local hot spots that encourage self-gasification of coke [16]. The surface area significantly reduced for reused catalyst after run 2.

3.2.3·NH3-TPD analysis

NH3-TPD analysis was used to determine the extent to which deactivation of catalyst has occurred. NH3-TPD analysis for fresh and used catalyst was conducted. Fresh HZSM-5 catalyst showed two distinct peaks. The peak at the lower temperature (160–190 °C) represents weak acid sites and the one at the higher temperature (330–360 °C) represents strong acid sites (Fig. 4).



* Reproduced from [24]

Fig. 4. NH3-TPD profiles for fresh catalyst and catalyst heated in induction, microwave and conventional reactor. *Reproduced from [23].

Our results indicated that coke deposition mainly occurs on the strong acid sites for catalytic upgrading activity. The peak for strong acid site (325–365 °C) was shown to disappear almost entirely for conventionally heated catalyst [23], marking the high amount of coke deposition. This peak was still reported for inductively heated catalyst, but with a largely reduced intensity. However, for the microwave heated catalyst, the peak intensity is only slightly reduced compared to the fresh catalyst (Fig. 4). The highest the peak is at the strong acid site, the greater is the aromatization effect; HZSM-5 has higher concentration of strong acid sites [39]. The rate of consumption of weak acid sites is lower compared to that of strong acid sites. These results are consistent with other studies reported in the literature for HZSM-5 catalyst behavior in time [29]. For the weak acid sites, the peak intensity reduces only slightly for microwave heating followed by inductively heated catalyst; it is decreased the most for conventionally heated catalyst [23]. Slight shift of peak toward left also indicates a decrease in the strength of acid sites due to coke deposition.

3.2.4. XRD analysis of catalyst

X-ray diffraction patterns of fresh and deactivated catalysts are shown in Fig. 5. Distinct peaks between 8.0–9.0° and 22–25° are observed for both fresh and deactivated catalysts. No significant changes in the crystal structure were observed for deactivated catalyst. However, the difference in peak intensity changed for both microwave and conventionally heated catalyst was significant when compared to fresh HZSM-5 catalyst at $2\theta = 8°$ and 23°. At $2\theta = 25°$ two distinct peaks are present for fresh catalyst, however,

Table 4
BET surface area and micropore volume for fresh and used catalyst.

Sample	BET surface area (m^2/g)		Micropore area (m^2/g)	Micropore volume (cm^3/g)
HZSM-5*	Fresh	247.7	196.4	0.0950
Microwave heating	Run 1	222.586	97.334	0.043
	Run 2	143.038	66.823	0.031
Inductive heating*	Run 1	210.7	143.4	0.0700
	Run 2	85.5	156.3	0.0690
Conventional heating*	Run 1	177.624	105.203	0.047
	Run 2	91.186	50.00	0.022

* Reproduced from [23].

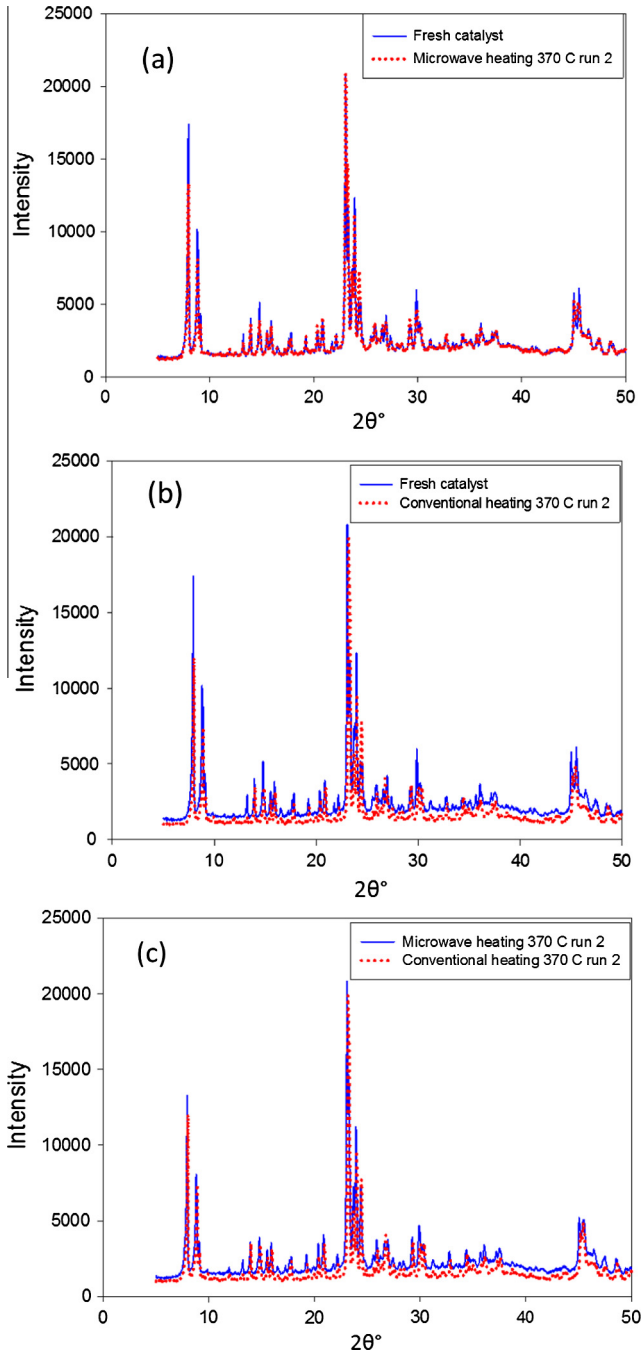


Fig. 5. XRD patterns of (a) fresh (blue) and microwave heated deactivated catalyst (red), (b) fresh (blue) and conventionally heated deactivated catalyst (red), and (c) microwave heated (blue) and conventionally heated deactivated catalyst (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

for deactivated catalyst for only one peak is observed for both microwave and conventional heating methods.

The peak intensity is low for conventionally heated catalyst compared to microwave heated catalyst (Fig. 5c). The crystallinity of sample was calculated from the characteristic area under the peaks at 23–25°. The peak area of fresh, microwave heated and conventional heated catalyst was 100%, 93.94% and 68.61% respectively. The change in intensity has been attributed to the removal of framework aluminum in the zeolite structure, as well as decrease in crystallinity [40]. This change in intensities could be associated with the coke deposition within the catalyst pores

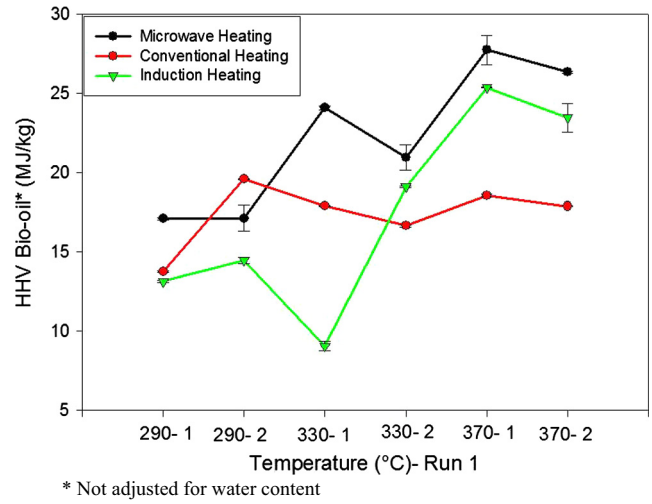


Fig. 6. High heating value of bio-oil (MJ/kg) for different heating methods. *Not adjusted for water content.

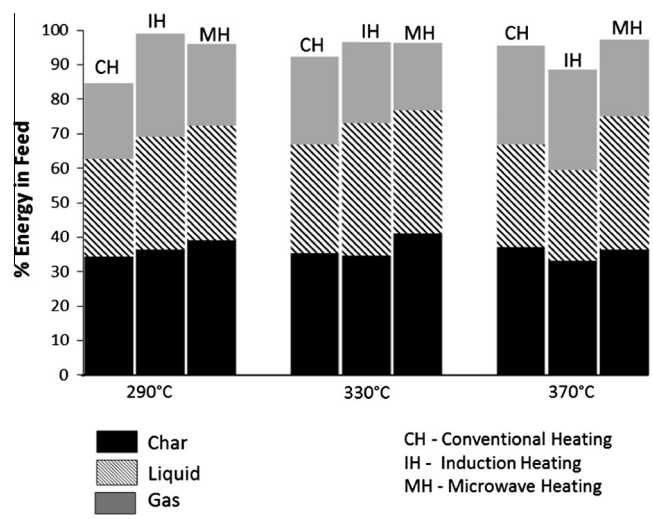


Fig. 7. Percent energy in feed contribution by liquid, char and gas yields for three heating methods.

[41]. However, it should be noted that the comparison is made based on relative peak positions and intensities of XRD patterns.

3.3. Heating value and energy balance

The high heating value (HHV) of bio-oil was measured using a bomb calorimeter as described in ASTM D200. The HHV of biomass, char and gas were also calculated based on the CHNSO elemental analysis using Dulong's equation [42]. The HHV for raw biomass was measured as 19.56 MJ/kg (ESI – Table S2). The bio-oil obtained from upgrading of pyrolysis vapors had a high heating value in the range of 15–27 MJ/kg depending on the catalyst bed temperature. The heating value increased as the catalyst temperature increased. Slightly higher heating values were noted for microwave heating process compared to other two methods (Fig. 6). The heating value for liquids was higher for run 1 compared to run 2. Highest HHV of 27.74 MJ/kg was obtained for microwave heating at 370 °C after 1st run. The typical heating value for non-upgraded pyrolytic bio-oil is 15–17.5 MJ/kg, we observed 25–30% increase in the heating values of bio-oil obtained, especially at catalyst bed temperature of 370 °C (Fig. 6).

HHV contribution of char was highest ranging from 31 to 33 MJ/kg; whereas heating value of gas ranged from 9 to

Table 5
Energy input and % efficiency of microwave heating.

Upgrading temperature (°C)	Power input for catalyst bed heating (MJ)			Decrease in energy input in microwave heating (%)	Increase in overall energy efficiency of microwave process (%)
	Conventional heating	Microwave heating	Induction heating		
290	0.6552	0.311	1.032	52.53	29.34
330	0.6552	0.3628	1.290	44.63	31.89
370	0.6552	0.4296	1.806	34.43	30.08

11 MJ/kg (Fig. 7). Although about 50% yield was obtained from gas, it was rich in CO_2 and hence yielded lower HHV values. Catalytic upgrading removes oxygen in the form of CO and CO_2 along with water on bio-oil, thus concentration of CO_2 was high, reducing the overall heating value of gas. Highest heating value contribution to gas was obtained from methane.

Microwave heating mechanism has an advantage of direct heating of material at a molecular level, which reduces heat losses associated with heat transfer between carrier and catalyst and increases process efficiency. With proper reactor design, a volumetric heating of catalyst bed with minimum temperature gradient can be achieved with microwave reactors. Together with low heat loss and a relatively easy control of temperature and its uniformity (with proper reactor design) microwave heating is a viable and energy efficient technique for catalyst bed heating. We determined the amount of power consumed for all three catalyst heating methods. Induction heating consumed the most power to heat the catalyst; 1.032 MJ at 290 °C, 1.29 MJ at 330 °C and 1.806 MJ at 370 °C (Table 5). However the heating rate was higher for induction heating compared to conventional heating.

The overall process energy balance was calculated based on the energy content of biomass and products, energy input for pyrolysis as well as catalyst heating. The energy efficiency of the process was calculated based on the total energy input for the process and the energy output received in the form of energy content of products (HHV values). Microwave heating was the most efficient process of all three. Use of microwave reactor for catalyst heating increased the process efficiency by 30% for all temperatures (Table 5). Microwave reactor also consumed least power and the percent energy input for microwave power was 35–50% lower when compared to conventional heating.

Overall, *ex-situ* microwave upgrading is a highly effective method for pyrolysis vapor upgrading. Temperature of the catalyst bed can be optimized independent of biomass pyrolysis temperature using the proposed *ex-situ* upgrading method. Microwave heating of catalyst has various advantages over conventional methods, delivering higher energy efficiency, low energy input, direct heating, and low coke deposition. Microwave heating could also lead in increased catalytic activity and rate of reaction. Scale up of microwave processes have been demonstrated in the food and agricultural industry, and can be successfully designed and implemented for biofuel production from renewable resources. With low coke deposition and high aromatic yield, microwave heating is a promising alternative to conventional reactors for biofuel upgrading.

4. Conclusions

An *ex-situ* microwave reactor was designed and operated for thermo-catalytic upgrading of pyrolysis vapors using HZSM-5. Microwave heating was found to be both effective and energy efficient compared to conventional and induction heating methods. Rate of deterioration of catalyst mainly due to coking was lower for microwave heating process. Higher aromatic hydrocarbon yield, lower oxygen content and high HHV value of bio-oil was obtained by microwave heating of catalyst. In principle, this heating technique can be used for thermo-catalytic reactions not limited to pyrolysis, provided the catalyst is a dielectric material, while full capacity of the reactor is yet to be completely realized, however, it holds the potential to improve the catalyst heating efficiency significantly and should be further studied for scale up applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apenergy.2016.09.047.

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