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Title: EFFECT OF WATER ADDITION IN A MICROWAVE ASSISTED THERMAL CRACKING OF BIOMASS TAR MODELS

Article Type: Research Paper

Keywords: Microwave irradiation; thermal cracking; water treatment; tar removal; toluene conversion.

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Abstract: Producer gas from biomass gasification is plagued by the presence of tar which causes pipe blockages. Thermal and catalytic treatments in a microwave reactor have been shown to be effective methods in removing tar from producer gas. A question arises as to the possibility of enhancing the removal mechanism by adding water into the reactor. Toluene and naphthalene were used as tar models in the present study with N2 as the carrier gas followed by the use of simulated producer gas. Thermal treatment with various amount of water was added at temperatures in the range of 800-1200□C. The tar removal efficiency obtained 95.83% at the optimum temperature of 1200□C for naphthalene in for toluene 96.32% at 1050□C at water to tar ratio (W/T) of 0.3. This study shows that the removal of tar by microwave irradiation with water addition is a significant and effective method in tar cracking.

Date: 4th November 2016

Editor,
Editorial Office
The Applied Thermal Engineering Journal
Elsevier Science Ltd.

Dear Sir,

Re: Effect of Water Addition in a Microwave Assisted Thermal Cracking of Biomass Tar Models

Herewith I attached the paper to be reviewed for The Applied Thermal Engineering Journal. This paper is our original unpublished work and it has not been submitted to any other journal for review and it is not under consideration for publication elsewhere. The paper describes a novel method for tar removal from producer gas using water addition in microwave tar cracking reactor.

Yours truly,

Prof. Dr. Zainal Alimuddin Zainal Alauddin
Corresponding author

Date: 23rd Jun 2016

Editor,
Editorial Office
The Applied Thermal Engineering Journal
Elsevier Science Ltd.

Dear Sir,

Re: Suggested Reviewers

Referring to the above subject, I would like to suggest the following reviewers:

- Professor Farid Nasir Ani, at the University of Technology Malaysia, E-mail address: farid@fkm.utm.my.
- Professor (Associate) Chungen Yin, at the Department of Energy Technology, Aalborg University. E-mail address: chy@et.aau.dk.
- Professor (Associate) Samsudin Anis, at the Mechanical Engineering, Universitas Negeri Semarang. E-mail address: samsudin_anis@yahoo.com.
- Professor (Associate) Mohammed Moustfa abdul almujeebu, at University of Dammam. E-mail address: mmalmujeebu@ud.edu.sa.

Yours truly,

Prof. Dr. Zainal Alimuddin Zainal Alauddin
Corresponding author

Responses to Technical Check Results

Date: 5th August 2016

Editor,

Editorial Office

The Applied Thermal Engineering Journal
Elsevier Science Ltd.

Dear Sir,

Thank you for your notes on the manuscript. All technical corrections were made as requested. The correction details are as following:

Issue 1:

Please provide Highlights. Highlights should contain 3 to 5 bullet points with a maximum of 85 characters per bullet point including spaces. Only the core results of the paper should be covered. Please ensure each bullet point is less than 85 characters. For more information and examples, please see: www.elsevier.com/researchhighlights.

Respond:

Research highlight file was attached with the manuscript.

Issue 2:

Table and Figure captions should be put on separate page at the end of the manuscript.

Respond:

Table and Figure captions were added on separate page at the end of the manuscript.

Issue 3:

The manuscript should be typed with double-line spacing.

Respond:

The manuscript was modified to double-line spacing.

Issue 4:

References should be numbered with Arabic numerals enclosed in square brackets. Please check.

Respond:

All references in the manuscript were corrected to the requested format.

Yours truly,

Prof. Dr. Zainal Alimuddin Zainal Alauddin

Corresponding author

Date: 4th November 2016

Editor,
Editorial Office
The Applied Thermal Engineering Journal
Elsevier Science Ltd.

Dear Editor,

Thank you for your useful comments and suggestions on the manuscript. We have modified the manuscript according to the reviewers' comments, and detailed corrections are listed below:

Reviewer 1

Issue 1:
Use proper symbol for degree centigrade throughout the manuscript Example: o C.

Response:
The symbol was replaced with a proper symbol for degree centigrade (°C) throughout the manuscript.

Issue 2:
In Equipment for experiment, sufficient explanation is needed to understand.

Response:
The "Equipment for experiment" title was changed to "Experimental procedure and equipment". This section was totally rewritten and the process and equipment use procedures were added to the equipment description to clarify the testing environment.

Issue 3:
In Equipment for experiment "A type K thermocouple was placed in a reactor to control the temperature. " How K type thermocouple can control the temperature. The sentence may be changed.

Response:
The statement (L. 133–136) was modified as following:

"Type-K thermocouple was placed inside the reactor to measure average bed material temperature. The thermocouple was connected to an external temperature controller (shinko Technos JCS-33A) that controls microwave power supply to maintain temperature at the desired value."

Issue 4:
Include a photographic view of experimental setup for better understanding.

Response:
A new figure (1) that includes a photographic view was added.

Issue 5:
An error analysis is required for the instruments used in the experiment.

Response:
Main measuring equipment for the experiment were: the sensitive electronic balance for tar and water weigh, thermocouples for temperature and GC–TCD for gas composition. The balance accuracy was ± 1 mg and with the samples in the range of 0.5–1 g, balance sensitivity had no effect on results stability. However, slight variation in weight during the addition process was inevitable, thus, maximum tolerance of ±5 mg was set for the added materials. As for the GC–TCD, certified calibration gas tanks were provided by the supplier to calibrate the area under the curve for each gas species. The following paragraph (L. 220–227) and Table 2 were added to discuss the experimental error analysis:

"All experiments were repeated a minimum of three times for experimental error analysis, and if the error exceeded 5%, the test was repeated further. Table 2 shows error analysis based on ± 1 standard deviation for thermal tar removal efficiency at different W/T ratios. It was noticed that the tar input mass tolerance had a significant effect on result stability, thus, maximum allowed tolerance was ± 5mg/0.5g. Other error factors showed less sensitivity such as the input mass of water and reactor temperature control were ± 5 °C variance did not show any considerable effect on result stability."

Issue 6:
Why SiC is used for bed. give proper explanation.

Response:
The following paragraph (L. 111–117) was added under the materials section (2.1): "Carbon based materials have the ability to absorb the emitted microwaves and convert it into heat. Thus, char coal is widely used in microwave tar thermal treatment since it acts as a natural catalyst additional to waves absorbing capability. However, the aim of this study is to investigate the effect of water addition on tar cracking at elevated temperatures. Therefore, any material with catalytic effect was removed, and silicon carbide (SiC) was selected as absorber due to its neutral effect on tar cracking [13]."

Issue 7:
What is Tar removal efficiency. It is not explained anywhere in the manuscript. Also W/T ratio also to be explained.

Response:
A new Equation (1) was added to define tar removal efficiency (L. 161).

The following statement was added (L. 162–163) to define W/T ratio:

“In order to study the effect of water on tar removal, the water to tar mass ratio (W/T) was varied from zero (i.e. no water) up to 0.5.”

Issue 8:
The volume of SiC affects microwave, but the volume of SiC used is not specified.

Response:
Equation (12) (L. 267) was added to clarify the relation between SiC volume and height. The equation is derived from the porosity or void fraction definition as follows:

If ϕ is the porosity fraction; Vt is the total volume; Vv is the void volume; V is the SiC volume; r is the reactor radius; h is the SiC height:

$V_t = V + V_v$ and $\emptyset = V_v/V_t$ then: $\emptyset = (V_t - V)/V_t = 1 - (V/V_t) = 1 - (V/\pi r^2 h)$

The following paragraph was added in L. 264–270:

“Bed height represents the absorber material volume for similar particle size and reactor diameter. Thus, for same SiC porosity, bed high is a direct indication of the SiC volume as can be illustrated from Equation (12):

$h = V/[\pi r^2(1 - \emptyset)]$ (12)

Where, ϕ is the porosity fraction; V is the SiC volume; r is the reactor radius; h is the SiC bed height.”

Issue 9:
Need clarity in the results and discussion.

Response:
Result and discussion (section 3) was totally rewritten. A new paragraph (L. 210–219) was also added as an introduction to the section to clarify the different variables in the study and experimental error analysis.

Issue 10:
In page no .11 ,in last paragraph symbol '<epsilon>' is repeated.

Response:
The paragraph (L. 312–314) was modified as follows:

“Where λ_0 is the free space wavelength of the microwave radiation and $\varepsilon''/\varepsilon'$ the ratio of the dielectric loss to the dielectric constant also known as the dielectric loss tangent (tan δ).”

Issue 11:
Check the references are in the journal format.

Response:
Reference list was checked and corrected in the journal format. Two duplicated references were removed.

Issue 12:
Add some recent papers in the references list.

Response:
Twelve new references were added [2, 17– 26, 28]

Reviewer #2:

Issue 1:
First, your manuscript would benefit from editing by a native English speaker before you submit a revised version in order to help clarify the major conclusions of your article. The recent version contains many errors in grammar.

Response:
The manuscript was sent to a language proof reading and was entirely rewritten.

Issue 2:
The font of unit of temperature should be corrected.

Response:
The symbol was replaced with a proper symbol for degree centigrade (°C) throughout the manuscript.

Issue 3:
The stability and reproduction of the experimental results should be well explained and give sufficient data to convince the reviewer and readers.

Response:
The following paragraph (L. 220–227) and Table 2 were added to discuss the experimental error analysis:

"All experiments were repeated a minimum of three times for experimental error analysis, and if the error exceeded 5%, the test was repeated further. Table 2 shows error analysis based on ± 1 standard deviation for thermal tar removal efficiency at different W/T ratios. It was noticed that the tar input mass tolerance had a significant effect on result stability, thus, maximum allowed tolerance was ± 5mg/0.5g. Other error factors showed less sensitivity such

as the input mass of water and reactor temperature control were ± 5 °C variance did not show any considerable effect on result stability."

Issue 4:
In section 2.3, What's LPM? The abbreviations must be defined at their first mention in the text.

Response:
Full definition (liter per minute) was added to the text before the abbreviation (L.176).

Issue 5:
In section 2.5, toluene, naphthalene, phenol and pyrene are compounds found in tar biomass. Only naphthalene and toluene tar models were considered in this study as they constitute the majority of tar in the producer gas. Please explain the reason of naphthalene and toluene rather than phenol and pyrene in more detail. What is the percentage of the of phenol and pyrene in biomass tar ?

Response:
Biomass tar sample obtained from rubber wood air gasification was analyzed in GC–MS and 32 tar species were identified. Phenol and pyrene yields were 4.82 & 11.07 (wt%) respectively. However, phenol and pyrene were not detected during thermal treatment at 800°C & 900°C respectively and were cracked at lower temperatures without the use of catalysts. Whereas, toluene and naphthalene required high temperature treatment in the range 1000–1200°C and even it cannot be fully cracked at high temperature without the use of catalytic materials. Therefore, toluene and naphthalene were selected as the main tar model materials to be studied separately to evaluate thermal treatment at high temperature range 900- 1200°C for each type.

The use of actual producer gas through the reactor and full GC–MS biomass tar analysis were included in another paper that will be published soon.

Issue 6:
Figure 2 shows Maximum temperature profile for various: (a) SiC particle zise, (b) height bed, (c) gas flow rate and (d) microwave power. Why just discuss the maximum temperature rather than average temperature? Please illustrates how to define and get the maximum temperature.

Response:
Recorded temperatures were for average values not the maximum. The intended meaning in the figure caption was the highest temperatures achieved at the four cases. Figure caption was modified to " Temperature profile for various: (a) …."

The following statement was added in "Methods" section (L. 133–134): "Type-K thermocouple was placed inside the reactor to measure average bed material temperature."

Issue 7:
The number of references is too small and most references are old.

Response:
Literature survey and reference list was updated with more resent and up-to-date references. Twelve new references were added [2, 17– 26, 28]

Issue 8:
Table captions are incomplete.

Response:
Tables 1 and 2 captions were checked.

Yours truly,

Prof. Dr. Zainal Alimuddin Zainal Alauddin

Corresponding author

Research highlights

- Effective tar thermal treatment with water addition using microwave is proposed.
- The reactor temperature of 1200^0C can be reached quickly at bed height 120 mm.
- The optimum water to tar ratio W/T was 0.3 for tar models.
- Temperature greatly effect tar removal at various W/T rates.

EFFECT OF WATER ADDITION IN A MICROWAVE ASSISTED THERMAL CRACKING OF BIOMASS TAR MODELS

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Abstract

Producer gas from biomass gasification is plagued by the presence of tar which causes pipe blockages. Thermal and catalytic treatments in a microwave reactor have been shown to be effective methods in removing tar from producer gas. A question arises as to the possibility of enhancing the removal mechanism by adding water into the reactor. Toluene and naphthalene were used as tar models in the present study with N_2 as the carrier gas followed by the use of simulated producer gas. Thermal treatment with various amount of water was added at temperatures in the range of 800-1200°C. The tar removal efficiency obtained 95.83% at the optimum temperature of 1200°C for naphthalene in for toluene 96.32% at 1050°C at water to tar ratio (W/T) of 0.3. This study shows that the removal of tar by microwave irradiation with water addition is a significant and effective method in tar cracking.

Keywords: *Microwave irradiation; thermal cracking; water treatment; tar removal; toluene conversion.*

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1. Introduction

One of the main downsides in utilizing biomass producer gas in internal combustion engines and gas turbines is the gas contamination with tar. Tar condensation can occur in pipelines and turbine engines at high concentration levels resulting in blockage in the intake manifold and valves as well as fouling effects on turbine blades. Tar contamination in producer gas is in the order of about 1, 10 and 100 gNm^{-3}, in downdraft, updraft and fluidized bed gasifiers respectively [1]. The recommended tar concentration in internal combustion engines and gas turbines are 100 and 5 mg Nm^{-3} respectively [1].

Primary tar removal by mechanical and catalytic treatments inside the gasifier did not show significant reduction in tar [2-5]. However, secondary tar removal outside the gasifier is preferred since tar is converted into additional energy without any production waste [6].

Thermal tar removal efficiency is considerably lower at temperatures below 1100 °C with longer residence time compared to higher temperatures [7-9]. Hence, significant tar removal can be achieved above 1200°C with shorter residence time below 10 s, but at the expense of higher energy consumption and cost [7-9].

Many early researches have investigated the effect of steam on tar formation and cracking through steam gasification. Some studies showed that the increment in steam concentration has resulted in a significant reduction of tar [10]. Also, in the presence of steam, hydrogen and methane products were almost five times higher than under pyrolysis conditions [11]. Tar formation from soot was also investigated where steam gasification of soot was found to be in the range of 1100-1400 °C [7, 8]. Steam gasification of soot reaches its maximum conversion rate at about 1250 °C and then the changes of the soot-structure into less reactive soot causes the steam

gasification of soot to stop at higher temperatures. Tar composition depends mainly on reaction temperature during steam reforming of tar. At reaction temperature of 750 °C, tar composition is relatively simple compared to the more complex tar formations at 950 °C that mainly consists of 4- and 5-ring aromatics [11].

The influence of hydrogen on thermal conversion of tar was also investigated. Hydrogen, on the one hand, inhibits polymerization by competitive inhibition and stimulates cracking reactions by increasing the driving forces. This directs the general thermal tar reactions away from polymerization and towards cracking. On the other hand, hydrogen-radicals react fast with unsaturated molecules, thus, any recombination of unsaturated molecules or reaction with carbon-containing radicals is inhibited. Because soot formation is suppressed, the total conversion, for example benzene and naphthalene, is decreased by the presence of hydrogen [7]. However, in the case of toluene conversion the presence of hydrogen can boost the rate of conversion [7, 12, 13].

Thermal tar treatment can be achieved by either the conventional heating or by microwave radio frequency heating. Conventional heating suffers from the high heat losses and the walls of the reactor can be easily damaged by continuous heating. Hence conventional heating for tar removal method is uneconomical and expensive [14]. Microwave irradiation can provide intensive, rapid and localized heating for the materials that can absorb radio frequencies through the molecular interaction of electromagnetic fields without heating the surrounding. Thus, volumetric heat treatment using microwave can reduce energy consumption significantly. The advantages of microwave technology for thermal treatment can be summarised as following: rapid heating, high temperature, heating selectively, increase in chemical reactivity, flexibility and ease of control, availability of the equipment, compactness

and portability, lower cost and maintenance, lower energy consumption [14, 15]. Microwave technology has been recently utilized in a wider range of applications such as in biomass pyrolysis for oil production [14, 16, 17] as well as syngas production [18, 19] and even in fast biomass gasification in the presence of an oxidizer [20].

Thermal and catalytic syngas tar cracking using microwave technology has been utilized widely as well. Wide range of catalytic materials that composes basically alkaline earth metal oxides and natural ores are used for tar reduction. Many researchers have investigated the use of dolomite, Y-zeolite [21, 22], bio-char [23] and bio-char with K and Ca [24] as catalysts, as well as silicon carbide (SiC) [21, 22] as micro wave radiofrequency absorbing material. Although the aforementioned studies investigated the cracking of tar contamination in syngas, only few used actual tar from biomass gasification [21]. Instead, most of the studies used tar model materials to simulate the different grades of biomass tar for better control over the quantities of tar vapours and tar conversion analysis. Common materials used as tar models are toluene [22-25], naphthalene, [22, 24], and phenol [24].

In this study the characteristics of thermal and catalytic tar removal with aid of a domestic microwave oven was investigated. A new approach of water addition in high temperature tar cracking was experimentally tested. It is hypothesised that the addition of water will not only increase in radical reaction and enhance the high temperature tar cracking, but also provide rapid heating with high electromagnetic irradiation intensity.

2. Methods

2.1. Materials

Toluene and naphthalene are the materials used as the tar model, which represents tar in the producer gas. Naphthalene ($C_{10}H_8$) is a light weight polycyclic aromatic hydrocarbon compound (LPAH) which is a class 4 tar, while toluene (C_7H_8) is a light, aromatic hydrocarbon (LAH) which is a class 3 tar [1]. Purified nitrogen (99.999% purity) was used as the carrier gas that carries the evaporate tar model to the reactor via insulated pipes.

Carbon based materials have the ability to absorb the emitted microwaves and convert it into heat. Thus, charcoal is widely used in microwave tar thermal treatment since it acts as a natural catalyst additional to waves absorbing capability. However, the aim of this study is to investigate the effect of water addition on tar cracking at elevated temperatures. Therefore, any material with catalytic effect was removed, and silicon carbide (SiC) was selected as absorber due to its neutral effect on tar cracking [13]. Four SiC granule sizes were compared: 2.085mm (F10), 1.765 mm (F12), 1.470 mm (F14) and 1.230 mm (F16) since the wave penetration depth has a significant effect on heat generation and temperature. The physical properties of SiC in accordance with FEPA-Standard 42-GB-1984 R 1993 and 42-GB-1986 R 1993 are shown in **Table 1.**

2.2. Experimental Procedures and Equipment

The experimental apparatus consists of a modified domestic microwave oven, tar removal reactor, tar model generator, mixer, tar collector and measurement system as shown in **Fig. 1**. A schematic diagram of the experimental apparatus is also shown in **Fig. 2**. A domestic microwave oven (Panasonic, NN-SM330 M) with

maximum output power of 700 W and a frequency of 2450 MHz was used. A cylindrical reactor of 25.4 mm inner diameter and 160 mm height was fabricated using alumina that can withstand temperatures of up to 1600°C. The reactor was vertically mounted inside the microwave oven and insulated with asbestos rope to minimize heat loss and to prevent excessive heating of the microwave walls.

Type-K thermocouple was placed inside the reactor to measure the average bed material temperature. The thermocouple was connected to an external temperature controller (shinko Technos JCS-33A) that controls microwave power supply to maintain temperature at the desired value. A micro-analytical balance model TB-413 with a precision of 0.001g was used to determine the mass of tar model compounds. A stainless steel tank 3 of 100 mm diameter and 120 mm height was used as tar-water vapour generator. Various ratios of water and tar model compounds were placed in this tank and evaporated at 250°C using LPG stove. The ratio of water to tar was manipulated in the range of 0.1-0.5. A pressurized nitrogen cylinder was used to provide nitrogen as a carrier gas. N_2 was allowed to pass through tank 3 mainly during sampling process to carry the tar-water vapour through the tar sampling train. Otherwise, N_2 gas was mixed with tar-water vapour in a stainless steel mixing tank 4 to carry the mixture through the reactor. Gas residence time through the reactor was varied from 1.8 s down to 0.04 s by changing N_2 flow rate. The temperature of the reactor was varied in the range of 800-1200°C. Asbestos rope was used to insulate all tanks and pipes to maintain vapour temperature above 200°C and to prevent water and tar vapours condensation.

Tar sampling train was used to measure the amount of tar in the gas before and after the reactor. It contained a series of six bottles of 100 mL capacity each. First two bottles were placed at atmospheric condition containing isopropanol

organic solvent to condense and absorb the tar. The next four bottles were immersed in a mixture of ice and salt to maintain a temperature of about –22°C to be able to condense tar compounds classes 3 and 4 [26]. Isopropanol was evaporated in a vacuum of 100 mbar and 55°C leaving solid tar at the bottom of the bottles. All bottles were weighed before and after the process and gravimetric tar yield was obtained by the difference between the initial and final weights of the tar normalized by the collected gas volume. Tar mass was measured in g/Nm^3 unit and tar removal efficiency was calculated from Equation (1):

$$\text{Tar Removal Efficiency } (\%) = [(\text{Tar mass in} - \text{Tar mass out}/\text{Tar mass in}] \times 100 \quad (1)$$

In order to study the effect of water on tar removal, the water to tar mass ratio (W/T) was varied from zero (i.e. no water) up to 0.5. Tar samples were analysed using Gas Chromatography– Mass Spectrometry (GC–MS) analyser with NIST MS 2.0 software. Gas flowing out of the sampling train was collected in sampling bags and analysed in Gas Chromatography – Thermal Conductivity Detector (GC–TCD) to quantify gas composition.

Additional experiments were carried out on simulated producer gas to investigate the effect of water addition at elevated temperature on gas composition and heating value. Simulated producer gas of 15% H_2, 20% CO, 15% CO_2, 5% CH_4 and 45% N_2 in a pressurized tank was used as the carrier gas with the optimum reactor conditions obtained from the previous experiments.

2.3. Data analysis

Main manipulative variables during experiments were:

- N_2 flow rate in the range of 2–15 liter per minute (LPM).
- Microwave power (135–700 W).

- Bed height position (40–120 mm).
- Particle size of the susceptor material (F10–F16).

The temperature inside the microwave reactor was recorded every 5 minutes for 20 minutes of irradiation using a 12-channel temperature sensor with a temperature data logger Model 69292-30.

H_2, CO, CO_2, CH_4 and N_2 gases were detected in the GC–TCD analysis while the C_2-C_3 hydrocarbons were not detected. For each test sample, the amount of H_2, CO, CO_2 and CH_4 were 85% of the total volume measured, while N_2 can be calculated from the results of H_2, CO, CO_2 and CH_4 for each experiment. Based on the amount of product gas conversion, toluene (C_7H_8) molar concentration was calculated using Equation (2), which is defined as the product of carbon gases (CO, CO_2, CH_4) divided by the carbon in the toluene. The molar concentration of hydrogen was calculated using Equation (3) and a number of other gases can also be determined in the same way [27].

$$C_7H_8(\text{mol }\%) = [FCO,\text{out} + FCO_2,\text{out} + FCH_4,\text{out}/7FC_7H_8,\text{in}] \times 100 \quad (2)$$

$$V(H_2) = [H_2/H_2 + CO + CO_2 + CH_4] \times 100 \quad (3)$$

2.4. Steam reaction models

Toluene, naphthalene, phenol and pyrene are compounds found in tar biomass. Equations (4–10) show the reactions of various tar models with steam to produce CO and H_2. These reactions are endothermic. Only naphthalene and toluene tar models were considered in this study as they constitute the majority of tar in the producer gas.

$$\text{tar} + H_2O \leftrightarrow CO + H_2 + \Delta H \quad (4)$$

$$C_7H_8 + 7H_2O \leftrightarrow 7CO + 11H_2 \quad \Delta H_{393K} = +881.7 \text{kJmol}^{-1} \quad (5)$$

$$C_{10}H_8+10H_2O\leftrightarrow 10CO+14H_2 \quad \Delta H_{393K} = +1177.8 kJmol^{-1} \quad (6)$$

$$C_{16}H_{10}+16H_2O\leftrightarrow 16CO+21H_2 \quad \Delta H_{393K} = +651.7 kJmol^{-1} \quad (7)$$

$$C_6H_6O+5H_2O\leftrightarrow 6CO+8H_2 \quad \Delta H_{393K} = +1834.7 kJmol^{-1} \quad (8)$$

$$CH_4+H_2O\leftrightarrow CO+3H_2 \quad \Delta H_{393K} = +209.4 kJmol^{-1} \quad (9)$$

$$CO+H_2O\leftrightarrow CO_2+H_2 \quad \Delta H_{393K} = -40.0 kJmol^{-1} \quad (10)$$

3. Results and Discussion

In this study, the effect of water addition on tar removal was investigated with conjunction with temperature effect. Therefore, other factors that can affect tar removal such as the use of charcoal as microwave absorber was avoided since char has a catalytic effect on tar cracking. Moreover, in order to achieve a controlled measurement of tar removal, actual producer gas with tar contamination was not used for tar removal measurement. Instead, tar model materials namely: toluene and naphthalene with steam were carried by nitrogen gas through the reactor. Additional experiments were carried out on simulated producer gas as the carrier gas with tar model materials at the optimum W/T of 0.3. The tests showed the effect of water addition at elevated temperature on producer gas compositions and heating value.

All experiments were repeated a minimum of three times for experimental error analysis, and if the error exceeded 5%, the test was repeated further. Table 2 shows error analysis based on ± 1 standard deviation for thermal tar removal efficiency at different W/T ratios. It was noticed that the tar input mass tolerance had a significant effect on result stability, thus, maximum allowed tolerance was ± 5mg/0.5g. Other error factors showed less sensitivity such as the input mass of water and reactor temperature control were ± 5 °C variance did not show any considerable effect on result stability.

3.1. The temperature profile

3.1.1. Effect of SiC particle size on temperature

SiC bed particles size was investigated first to study the effect of particle size on microwave thermal heating performance as shown in **Fig. 3a**. Four sizes: F10, F12, F14, and F16 were tested while fixing other variables at 700 W input power, 10 LPM N_2 flow rate, and maximum bed height of 120 mm. After about 15 minutes, the bed temperature reached a steady state at 1206°C, 1196°C, 1179°C, and 1168°C for F16, F14, F12, and F10 respectively. The rates of heating were in the following order: 54.82°C min^{-1}, 54.54°C min^{-1}, 54.06°C min^{-1}, and 52.56°C min^{-1}, respectively. The smallest size F16 resulted in the highest heating rate and temperature compared to the other sizes. However, its effect on heating rate was not significant while the temperature difference was more noticeable at around 38 °C difference between maximum and minimum particle sizes.

The effect of the transmitted microwaves though SiC absorber converts the waves into heat energy mostly at the material surface, while the effect decreases exponentially through the depth (z) of the material as illustrated in Equation (11):

$$P(z) = P_0 e^{-\alpha z} \quad (11)$$

Where P_0 is the heat energy at the surface, P(z) is the energy at distance (z), and α is the attenuation constant. Therefore, smaller particle sizes are desirable to reduce the required heating power and to reach higher temperatures. Another advantage for the pulverized absorber materials is the friction between the particles caused by the wave vibrating effect, although the generated heat is insignificant. On the other hand, particle size is inversely proportional to the porosity, and reducing

particle size will cause a significant elevation in the flow pressure drop that will require more energy to push the gas through the reactor.

3.1.2. Effect of Bed Height

Microwave heating performance was further characterized by varying the SiC bed height while fixing other variables at 10 LPM N_2 flow rate, F16 SiC particle size and 700 W power input. Three bed heights of 40 mm, 80 mm, and 120 mm were tested as shown in **Fig. 3b**. It was noticed that temperature trend is almost linearly proportional with the bed height. Also, heating rate was significantly affected by the bed height since maximum height required about 15 minutes to reach steady state while minimum high was delayed for about 5 minutes.

Bed height represents the absorber material volume for similar particle size and reactor diameter. Thus, for same SiC porosity, bed high is a direct indication of the SiC volume as can be illustrated from Equation (12):

$$h = V/[\pi r^2(1-\emptyset)] \quad (12)$$

Where, ϕ is the porosity fraction; V is the SiC volume; r is the reactor radius; h is the SiC bed height. SiC absorber volume is directly proportional to the heat addition, which in turn translates directly in to height bed temperature as illustrated in Equation (13) [14].

$$P_{abs} = 2\pi p f \varepsilon_0 \varepsilon" E^2 V \quad (13)$$

Where, P_{abs} is the required microwave power (W), f is the frequency (Hz), ε_0 is the permittivity of free space (8.85 x10-12Fm 1), ε″ is the dielectric loss factor, E is the electric field (V m^{-1}), and V is the volume of the material (m^3). Another

advantage of the increased height is the minor addition of head caused by friction between bed particles.

3.1.3. Effect of N_2 Flow Rate

Flow rate through the reactor is a significant variable for evaluating heating performance since it governs the residence time. Flow rate is restricted by the bed material porosity and pressure drop in any practical system with an air blower to push the gas through the reactor. However, in order to get the unique effect of each variable, bed particle size variable was tested independently from the gas flow rate by using pressurized N_2 source to overcome pressure drop through the reactor. The effect of various N_2 flow rates in the range of 5-15 LPM were studied while fixing other variables such as the maximum bed height of 120 mm, F16 SiC particle size and 700 W power input as shown in **Fig. 3c**.

It can be noticed that by increasing flow rate through the bed particles up to 15 LPM, faster temperature distribution was achieved. Thus, temperature uniformity and steady state were achieved after 10 minutes compared to 15 minutes for lower flow rates. However, the cooling effect of higher flow rate has limited the temperature below 1000°C. On the other hand, cooling effect at lower flow rates was insignificant resulting in a low temperature difference between 5 and 10 LPM with slightly higher temperature of about 1220°C for the latter.

3.1.4. Effect of Microwave Power

Microwave power input is the primary variable that dictates bed temperature with almost linear relation as shown in. **Fig. 3d**. Other variables were fixed at optimum values of 120 mm bed height, 10 LPM N_2 flow rate, and particle size of

F16. The power of microwave absorption is strongly influenced by the electric field, thus, in order to accelerate heating process, high electric field is required. Heating rate and the time required to reach steady state is heavily influenced by the bed height and gas flow rate. However, for highest temperature at steady state, power input and bed height are the most influencing variables followed by gas flow and to a lesser extent the absorber particle size.

The effect of microwave penetration depth depends on the dielectric properties of the SiC material, as shown in Equation (14) [22].

$$Dp = \frac{\lambda o}{2\pi\sqrt{2\varepsilon'}}\left[\sqrt{1+\left(\frac{\varepsilon''}{\varepsilon'}\right)^2}-1\right]^{-1/2} \quad (14)$$

Where λ_0 is the free space wavelength of the microwave radiation and $\varepsilon''/\varepsilon'$ the ratio of the dielectric loss to the dielectric constant also known as the dielectric loss tangent (tan δ). At a fixed frequency, the dielectric property of tan δ depends on the temperature. SiC used in this study has a loss factor of 1.71 at room temperature and a frequency of 2.45 GHz. Therefore, the penetration depth of the microwave power in the material has a significant effect on the temperature inside the reactor.

Heat generation in the microwave reactor is due to transfer of electrons through a conductor, giving rise to electromagnetic waves. Hence, the number of electrons that flow determines the heat generation and temperature, and highest temperature is obtained at maximum power.

3.2. Effect of Water-Tar Ratio on Tar Removal Efficiency

Tests were performed with and without the water addition, and the highest tar removal efficiency was found to be 96.3% at 1050 °C and W/T of 0.3 for toluene as shown in **Fig. 4a**. The effect of water addition to a certain W/T ratio seems to be

caused by the ions and free radical formation at elevated temperature that causes tar molecules to adhere and cracked.

As for naphthalene, the highest tar removal efficiency was 95.83% at 1200°C and W/T of 0.3 as shown in **Fig. 4b**. Naphthalene compound (C_7H_{10}) reacts with H_2O to produce H_2 and CH_4 with no formation of coke/soot.

It can be noticed that both temperature and W/T ratio have shown significant effects on tar removal efficiency. At a certain temperature water and tar compounds are released and formed free radical compounds, hence, forming a new compounds.

Temperature effect on light PAH which is 2-3 rings compounds (LPAH) and heavy PAH which is more than 3 rings compounds (HPAH) during the microwave thermal treatment was investigated. At elevated temperatures, hydrocarbons will grow to form PAHs and ultimately forming soot and gases particularly H_2. Results show that the difference between toluene and naphthalene in terms of temperature effect and conversion yield of light and heavy PAHs are significant. **Fig. 5a** shows the process of LPAH and HPAH formation in toluene tar model in the temperature range of 950 – 1050°C. LPAH reaches maximum yield as the reaction temperature increases to 1000°C, then the yield starts to drop as more LPAH is converted into soot at higher temperatures. On the other hand, HPAH formation is more consistent with temperature with more HPAH compound found in the tar at higher temperatures. As for the naphthalene tar model, LPAH and HPAH behaviour with temperature is quite different as shown in **Fig. 5b**. At 1100 °C LPAH and HPAH yields were high but at elevated temperature, and most of the naphthalene compounds were converted at 1200 °C into soot as conformed by other researchers [7, 8].

3.3. Gas composition and heating value

For the final set of experiments, N_2 carrier gas was replaced with simulated producer gas that was mixed with tar model and steam at optimum W/T ratio before passing through the reactor. Producer gas thermal treatment through the reactor converted tar into useful form of combustible gases that elevated the low heating value (LHV) of the gas. Reactor temperature was set in the range of 800–1200 °C and producer gas out of the reactor was passed through the sampling train and then collected for GC–TCD analysis to determine the gas composition and LHV.

Fig. 6 a &b show the measured producer gas composition and LHV for different reactor temperatures for toluene and naphthalene. At elevated temperatures, many endothermic reactions can take place such as the wet forming reactions shown earlier for steam reaction model. Thus, C_7H_8, $C_{10}H_8$, CO, H_2, and even CO_2 react in the presence of steam to form syngas (i.e. CO and H_2) and CH_4. Moreover, endothermic dry forming of syngas by consuming CO_2 and CH_4 is another way to reduce CO_2 concentration in the producer gas. Hence, a noticeable increment in gas LHV was achieved mainly by reducing the inert CO_2 and increasing H_2 and CH_4consentrations. In actual producer gas, another contamination in the gas is the particle content. Particles are mostly comprised of char and soot and can contribute as well in elevating LHV by forming CO through partial oxidization at high temperature.

Water addition to the simulated producer gas has shown a significant enhancement in gas quality by 17.03% and 16.71% elevation in LHV for toluene and naphthalene, respectively, as shown in **Fig. 7a**. Moreover, water addition has shown improvement in tar removal efficiency over the dry heating tar removal method as

shown in **Fig. 7b**. Maximum tar removal efficiency at the optimum reactor conditions was about 96.83% and 95.01% for toluene and naphthalene respectively.

4. Conclusions

Microwave heating for tar removal provides fast and effective heat delivery with less energy consumption compared to the conventional heating methods. Bed height of 120 mm, N_2 gas flow rate of 10 LPM, and a microwave power of 700 W were the optimum reactor conditions. The optimum water to tar ratio W/T was 0.3 for both naphthalene and toluene tar models. Highest tar removal efficiency was found to be 96.3% at 1050 °C for toluene and 95.8% at 1200°C for naphthalene. Soot was not found during the tar removal thermal treatment of toluene and naphthalene with water addition. Simulated producer gas was used with the tar models to study the effect of water addition at elevated temperature on gas compositions and quality. A drop in CO_2 and elevation in H_2 concentrations was noticed due to the high temperature steam reaction with the producer gas. Also, a significant enhancements of the gas LHV and tar removal efficiency were achieved by adding water to the reactor. Maximum LHV and tar removal efficiency were 17.3% –16.71% and 96.83% – 95.01% for toluene and naphthalene, respectively.

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Table captions:

1. **Table 1.** Density and grain size distribution of silicon carbide (SiC)
2. **Table 2.** Samples of the experimental error analysis for thermal tar removal at minimum and maximum temperatures

Figure captions:

1. **Figure 1.** Experimental apparatus setup
2. **Figure 2.** A schematic diagram of the experimental apparatus
3. **Figure 3.** Temperature profile for various: (a) SiC particle size, (b) height bed, (c) gas flow rate and (d) microwave power
4. **Figure 4.** Removal efficiency optimum ratio water: (a) toluene and (b) naphthalene remove tar model of toluene on an optimum ratio of water-tar (W/T): 0.3
5. **Figure 5.** Tar compounds contained in condensed products during thermal treatment of tar models as a function of temperatures: (a) toluene and (b) naphthalene
6. **Figure 6.** Gas content and LHV for thermal treatment with tar model: (a) toluene and (b) naphthalene
7. **Figure 7.** (a) LHV (b) Tar removal model at thermal treatment without and with water

Table 1

Table 1. Density and grain size distribution of silicon carbide (SiC)

Grit designation (FEPA standard)	Bulk density (g/cm^3)	Grain size distribution		
		(μm)	(%)	Mean (μm)
F10	1.48	3350	0	2085
		2360	19	
		2000	52	
		1700	78	
		1400	81	
		<1400	0	
F12	1.53	2800	0	1765
		2000	8	
		1700	48	
		1400	87	
		1180	91	
		<1180	1	
F14	1.55	2360	0	1470
		11	11	
		1400	64	
		1180	85	
		1000	89	
		<1000	0	
F16	1.56	2000	0	1230
		1400	17	
		1180	48	
		1000	8	
		850	83	
		<850	0	

Table 2

Table 2. Samples of the experimental error analysis for thermal tar removal at minimum and maximum temperatures

Tar model	W/T	Reactor temperature (°C)	Tar input weight (mg)	Tar removal efficiency (%)
			Error (±1SD)	Error (%)
Toluene	0	850	±0.6	0.44
	0.1		±1.5	1.2
	0.2		±1.0	1.96
	0.3		±0.9	2.67
	0.4		±4.5	3.47
	0.5		±3.1	3.84
	0	1050	±3.5	3.87
	0.1		±1.89	0.8
	0.2		±4.03	3.0
	0.3		±4.2	3.9
	0.4		±2.05	0.4
	0.5		±2.1	2.14
Naphthalene	0	800	±3.3	4.44
	0.1		±1.0	0.08
	0.2		±2.5	0.5
	0.3		±2.5	3.21
	0.4		±1.4	2.35
	0.5		±2.2	2.32
	0	1200	±3.4	4.5
	0.1		±2.5	2.47
	0.2		±4.5	2.9
	0.3		±1.8	2.25
	0.4		±1.0	0.3
	0.5		±3.3	1.73

Figure 1

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Figure 2

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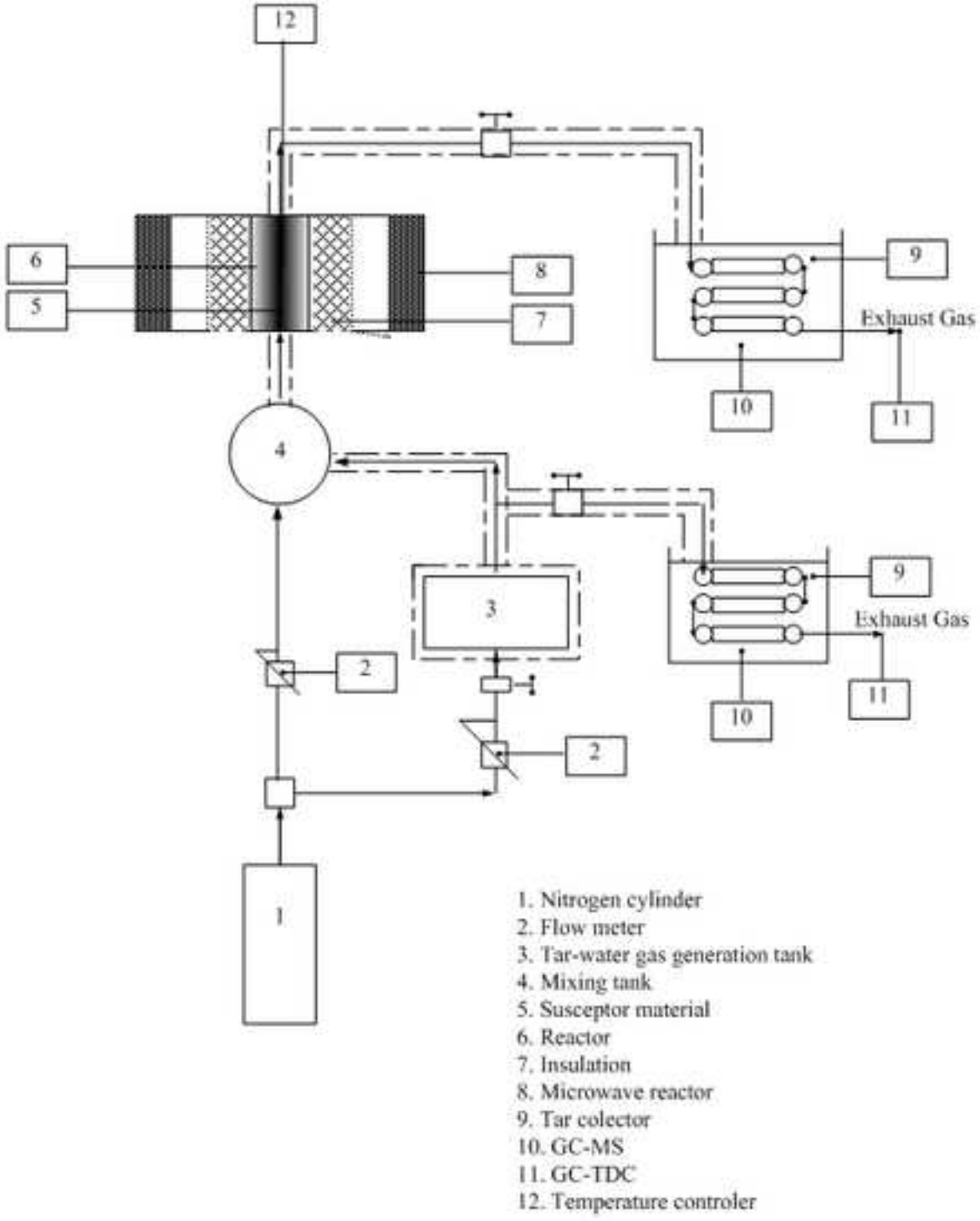

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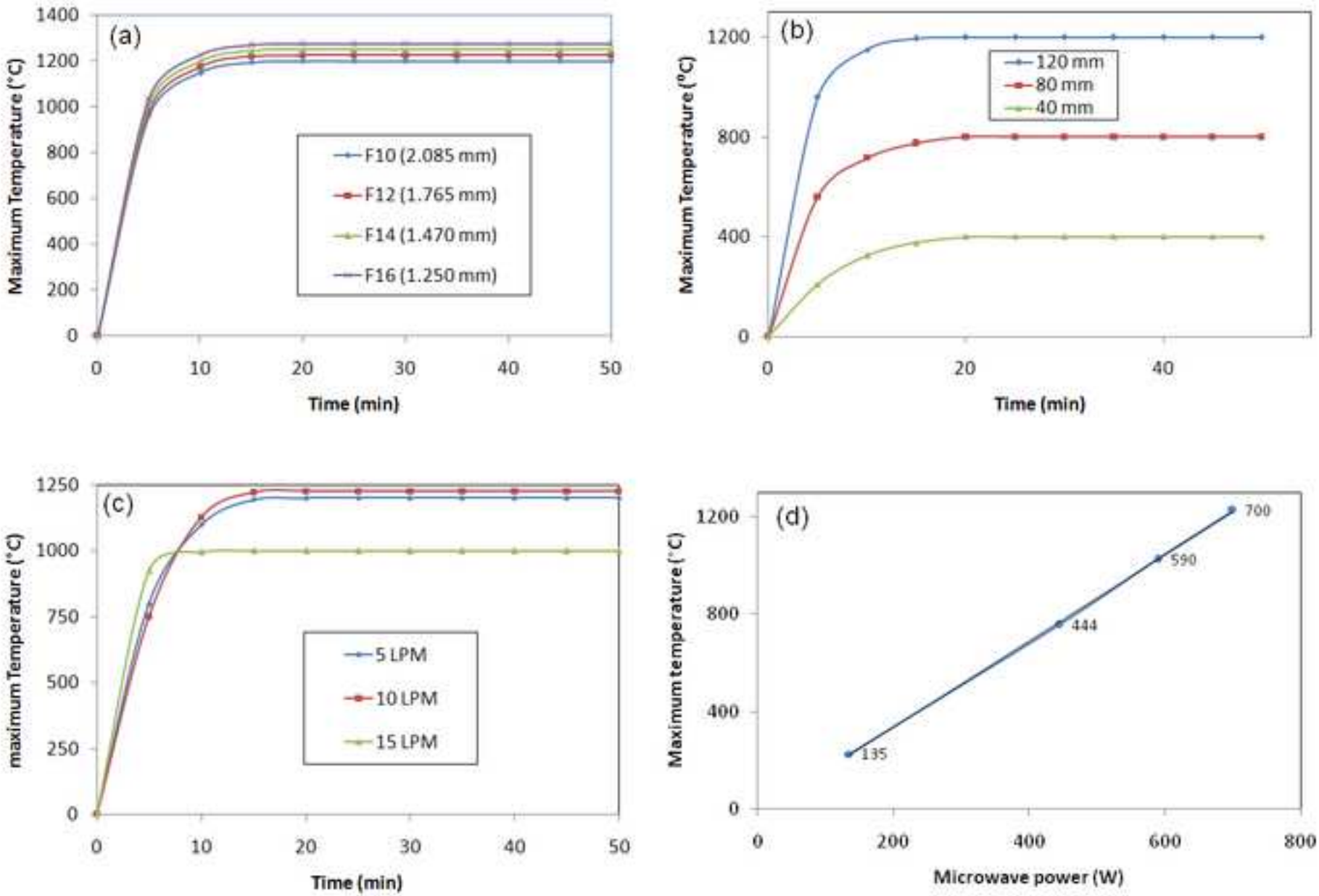

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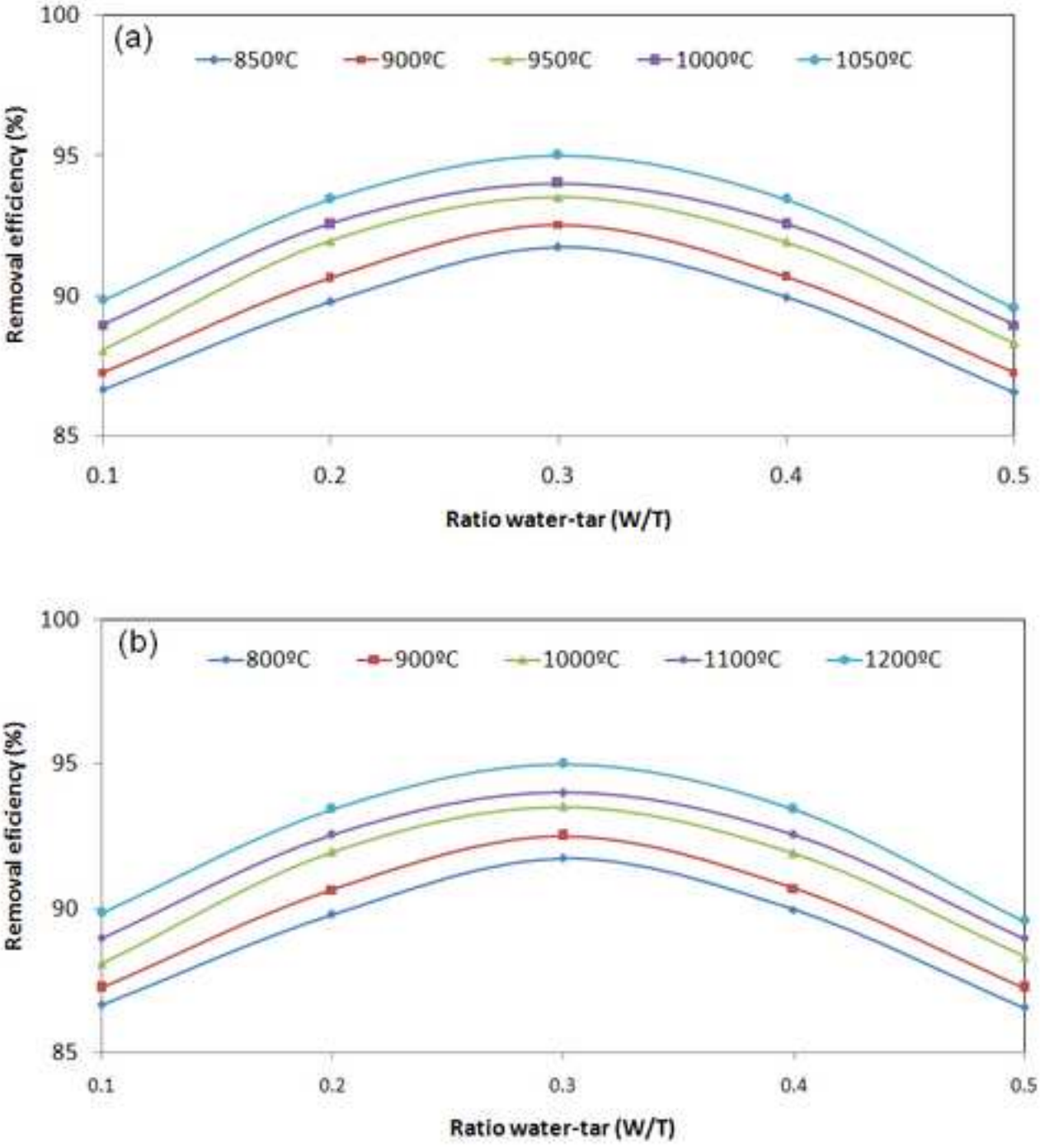

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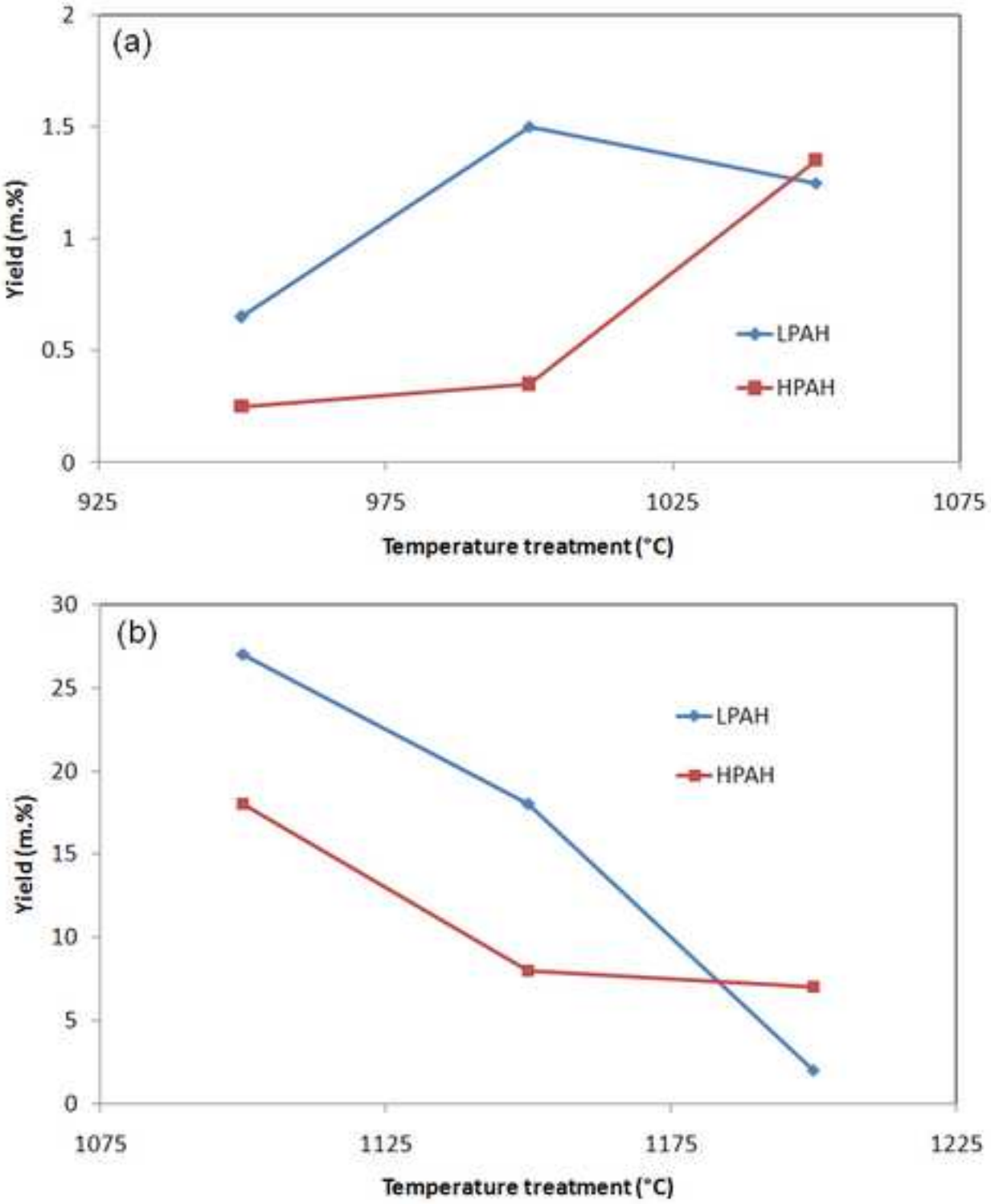

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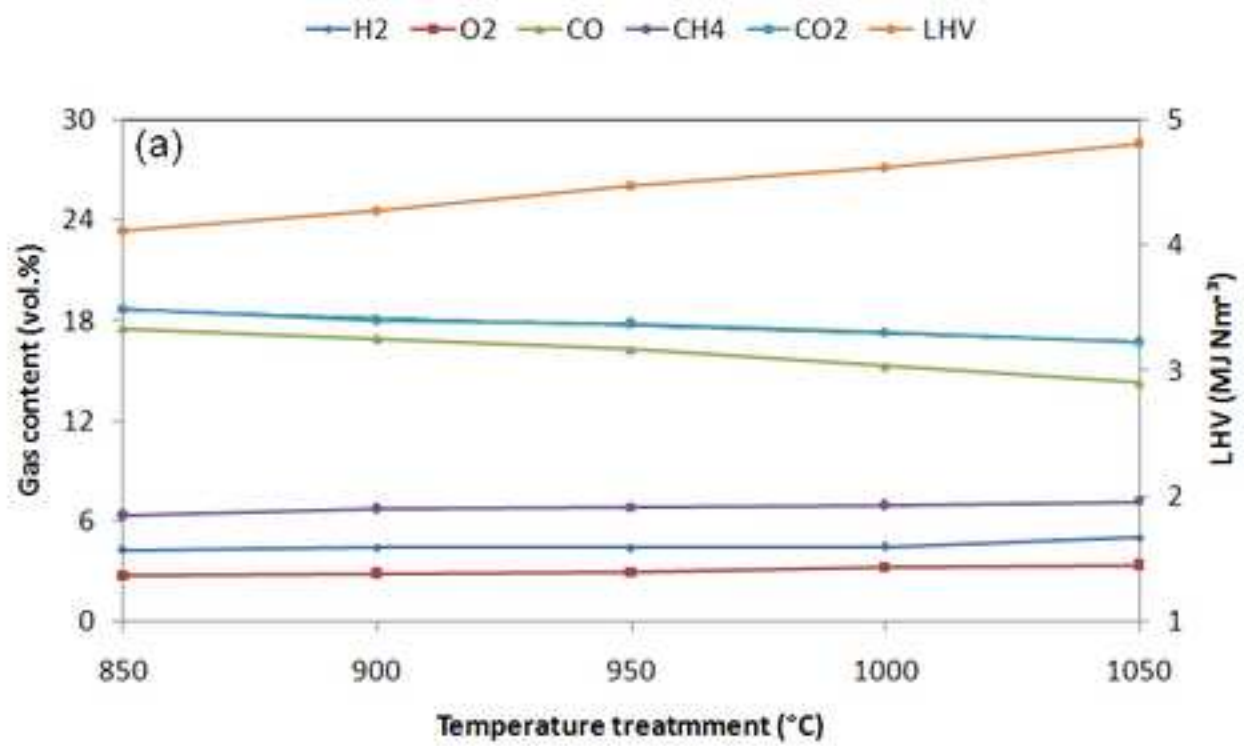

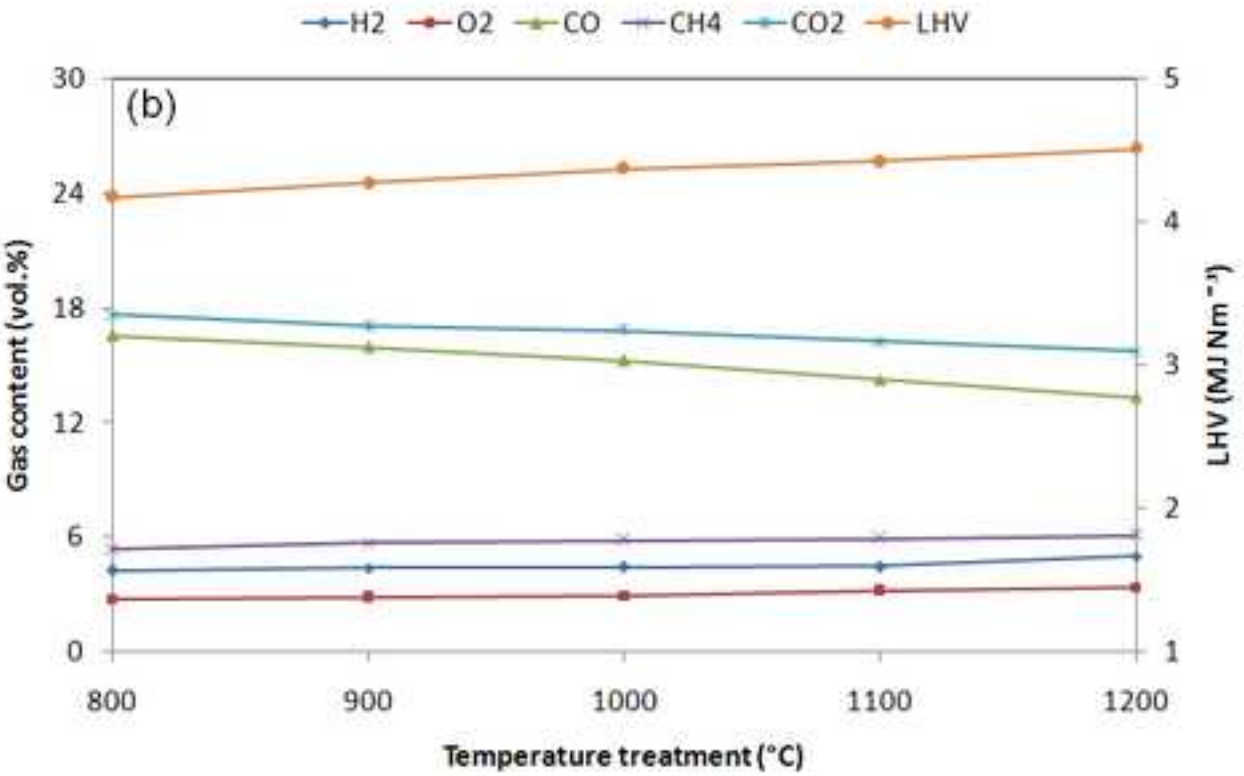

Figure 7

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