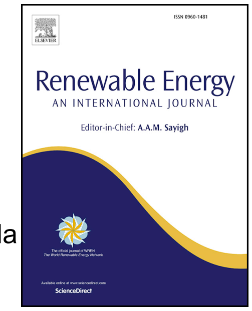

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Effect of different pre-treatment methods on gasification properties of grass biomass

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Abstract

The effects of different pre-treatment methods on the gasification efficiency of grass biomass have not previously been evaluated. In this study, the effect of three different pre-treatment methods on gasification properties of grass biomass was investigated under CO_2 conditions. The pre-treatment methods were dry torrefaction, wet torrefaction, and leaching (chemical). The results obtained showed that the heating values increased by 2.77 % in the leached grass, by 8.30 % in the dry torrefied grass and by 13.50 % in the wet torrefied grass. The surface area increased by almost a factor of 1.36 when the grass biomass was leached and increased by a factor of 1.14 when it was dry torrefied and by a factor of 70 in wet torrefaction. The pore volume increased by almost a factor of 1.20 when the grass biomass was leached and increased by a factor of 1.07 when it was dry torrefied and by a factor of 14.77 in wet torrefaction.

The gasification reactivity index increased by almost a factor of 8 when the grass biomass was leached and increased by a factor of 26 when it was dry torrefied and by 70 wet torrefactions. The activation energy of raw grass biomass was reduced from 161.70 kJ/mol to 141.50 kJ/mol for leached grass, 124.30 kJ/mol for dry torrefied and 86.97 kJ/mol for wet torrefied grass.

These results showed that there was more significant improvement in the gasification properties via wet torrefaction than in dry torrefaction and leaching. The research has provided some useful insights on the effects of different pre-treatment methods on grass biomass gasification properties

Keywords: Biomass, Gasification properties, Grass, Torrefaction, Leaching

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1. Introduction

Biomass as a source of energy represents a promising alternative to fossil fuels [1]. This is because biomass is available in abundance, renewable, sustainable, and carbon neutral [2]. South Africa has extensive biomass that is currently under-utilized or untapped for energy production. Of the biomass available, grass biomass appears to be the most imperative in terms of technical and economic feasibility [3]. Grass biomass can be converted into energy through thermochemical and biochemical processes [4]. A considerable number of researchers describe gasification as the most promising and efficient thermochemical process to convert biomass into useful gaseous fuels (such as CO, H_2, CH_4, etc.) under an oxygen restricted environment [5]-[7]. However, the inherent fuel characteristics of grass biomass compared to that of fossil fuels such as coal renders them unfavourable for energy production through gasification[7,9].

Grass biomass has high moisture content, low heating value, low bulk densities and recalcitrant structure and as a result improving the gasification efficiency of grass biomass remains a significant challenge [13]. Moreover, the presence of inorganic elements in grass biomass creates several technological problems and reduces the process efficiency during thermochemical conversion of biomass [14]. The problems that are caused by inorganic elements cause an increase in maintenance and operating cost of the process [15]. Therefore, modifying the recalcitrant structure and the removal of inorganic elements is definitely considered as a dominating step in the whole streams of the gasification process [16]. Previous researchers reported that the pre-treatment of biomass such as torrefaction of biomass, biological and chemical pre-treatment of biomass could improve the biomass conversion efficiency by improving their fuel properties [15]-[17].

According to Kostas *et al*., [15] pre-treatments serve a purpose of reducing the recalcitrance of biomass and modifying its structure; making the substrate more cooperative for conversion into a final product. It also increases the pore size and the overall surface area for reaction and subsequently making the diffusion of the reactant easy. Kirubakaran *et al*., [16] stated that when the biomass is less porous, the reaction only takes place on the exterior surface and as a result, this surface shrinks with the reaction. Dry torrefaction has been extensively investigated as a pre-treatment method prior to gasification of a woody biomass [17], [18], non woody biomass [19],[21] and starchy food waste [22] and the torrefaction temperature range is 200 to 300 °C [23],[24].

A recent study by Tsalidis *et al.*, [25] investigated the effect of torrefaction on the process performance of oxygen-steam blown CFB gasification of hardwood and softwood. The results proved that torrefaction played a significant impact on gasification performance of both feedstocks leading to decreasing the cold gas and carbon conversion efficiencies. In addition, Fan *et al.*, [24] also assessed the effect of torrefaction pre-treatment on the syngas production and tar formation from chemical looping gasification (CLG) of biomass over different oxygen carriers. The results showed an increase of the gas yield by 27.5 % with the reduced tar content from 43.6 to 17.6 g/Nm^3. Although dry torrefaction has been attested to be a promising pre-treatment for enhanced thermochemical process efficiency, large amounts of ash remained in biomass sample after being torrefied [23]. Wet torrefaction and leaching methods can remove some of the inorganic ash forming minerals and hence produce cleaner solid fuels, in comparison to dry torrefaction. Wet torrefaction is conducted in hot compressed water in the temperature within 150– 260 °C [26]. The process pressure is usually slightly higher than the saturated vapour pressure at the corresponding temperature. Wet torrefaction is very much suitable for wet feedstocks, which include forest residues, wet agricultural wastes, and aquatic energy crops. In addition to the main solid product, wet torrefaction also produces liquid by-products including water soluble and insoluble organic compounds, which can be further treated for the production of biogas, liquid fuels and/or valuable chemicals [27]. On the other hand, chemical pre-treatment known as leaching is performed in the presence of solvents, including acidic solution, alkali solution and organic solvent. It is normally carried out at a relatively low temperature (30-85 °C) compared to both dry and wet torrefaction. Leaching leads to the removal of alkali metals and alkaline earth metals from the fuel source and subsequently further reduces fouling and slagging [28]. In addition, leaching has a potential to reduce corrosion, emissions of acidic pollutants and the formation of toxic species generated during thermal processing [27]-[34]. Several studies have been done on leaching of alkali metals and inorganics, more often for pyrolysis and only few have been performed for combustion and gasification. Link *et al.*, [35] investigated the effect of leaching natural and artificial pre-treatment on the gasification of wine and vine (residue) biomass. The results showed that CO and H_2 content in the product gas were higher in leached vine residue in comparison to an untreated vine. Moreover, it was reported that the tar content of a leached vine was lower than that of the untreated. To the author's best knowledge, most research on upgrading the biomass fuel properties for gasification efficiency have been conducted on dry torrefaction and none has compared the effects of dry, wet torrefaction and leaching (acetic acid chemical) on gasification properties. Thus, this study compares the effect of dry torrefaction, wet torrefaction and acid leaching on both the properties of grass biomass and gasification efficiency of the grass biomass.

2. Material and methods

2.1.Biomass

The grass used as feedstock for this study was collected from the University of Johannesburg, South Africa. Dirt and contaminants from the grass were removed by water washing methods. The grass was then milled to a size of less than 200 µm by using a Retsch SM 200. Prior to each experiment, the characteristics of biomass such as ultimate and proximate (ASTM D4442), and SEM analyses were done.

2.2.Ultimate and proximate analysis

Proximate and ultimate analysis of raw and pre-treated grass were performed, and the results are presented in Table 1. Moisture content (MC), Volatile content (VC) and Ash content (AC) were determined using ASTM standard. Fixed carbon (FC) was calculated from the difference of MC, VC and AC content. The mass yield (M*y*) and energy yield (E*y*) of solid products were calculated using equation (1) and equation (2) respectively.

$$M_y\,(\%) = {M_{pre}}/{M_{raw}} \times 100 \qquad (1)$$

$$E_y\,(\%) = {M_y \times CV_{pre}}/{CV_{raw}} \times 100 \qquad (2)$$

M_{pre} and CV_{pre} are the mass and calorific value of pre-treated grass. M_{raw} and CV_{raw} are the mass and calorific value of raw grass, and CV_{pre}/CV_{raw} is energy density of the pretreated grass. The hydrogen, carbon and oxygen were assessed using a Thermo scientific flash 2000 CHNS-O analyser. The Calorific values (CV) raw and pre-treated grass were determined per BSI standard EN 14918 using e2k bomb calorimeter, in which 0.50 g of raw and pre-treated biomass was completely combusted under a pressurized O_2 atmosphere (3000 kPa).The morphology of samples were investigated by a field emission scanning electron microscopy (SEM, Japan Electronics Co., Ltd., JSM-7600F type). The specific surface area and pore size analyzer (BET, United States Mike Instrument Co., ASAP2020 type) was employed in further analysing the physical characteristics of the raw and treated grass biomass.

2.3.Wet torrefaction

Wet torrefaction (WT) was conducted in a 750 ml laboratory scale stainless steel (SS 316) autoclave reactor. For each trial, 25 g of biomass and 450 mL of deionized water was placed in the autoclave and sealed. To create an inert atmosphere, the reactor was flashed with nitrogen at 100 ml/min for 10 min. The reactor was heated from ambient temperature to the set torrefaction temperature (200 °C). Each test was carried out for about 60 min. After the completion of the experiment, the autoclave was internally cooled until the reactor temperature reached 30 °C. The solid-liquid mixture from the autoclave was collected and separated by filtration. The solid, i.e., the wet torrefied biomass was dried at 105 °C and weighed after drying to calculate the solid yield.

2.4.Dry torrefaction

This process was carried out in a horizontal quartz tube reactor. The weight of the feed tray was determined before and after filling it with the sample and two of the readings were recorded. The tank that supplies nitrogen to the furnace was opened just before running the furnace. A rectangular crucible was loaded up with around 1 g of grass biomass. The sample was placed in the middle of the reactor and then the reactor was inserted inside the furnace. The flowrate of Nitrogen was adjusted to 150 ml/min, heating rate to 10 °C/min and temperature to 250 °C and residence time at 40 min.

2.5.Leaching

The leaching experiments were carried out in 1 L, three neck flasks. A total of 400 mL of leaching solution (99.5 % Acetic acid) was added to the flask, and 25 g of dry biomass was added to this solution. The flasks containing biomass and leaching solution were heated using magnetic hot plates with a stirring speed of 250 rpm. The reactor was heated to the selected operating temperature of 85 °C. The treatment was carried out for 60 min. After the investigated time of leaching was attained, the reactor was cooled at room temperature by switching off the heating device for about 15 min. When the slurry (solution plus biomass) reached room temperature, the reactor was opened, and biomass and leaching liquid was separated by means of filtration (sieves were used). The change in the acidity of the liquid was measured to observe any difference during leaching. Thereafter, the biomass was then washed with de-ionized water to remove the remaining solid biomass /biochar residues from the leaching liquid, with the biomass dried at 105 °C for 24 h to remove all moisture.

2.6. CO_2 gasification: TGA

Thermogravimetric analysis (TGA) is one of the most used techniques to investigate kinetics of gasification of solid materials, such as biomass, petroleum coke, coal chars. In this study, the tests were carried out on a thermogravimetric analyser (STA 2500 regulus, NETZSCH, Germany). At the beginning of each experiment, approximately 5 mg of biomass or biochar was placed in a platinum crucible. The temperatures for this isothermal CO_2 gasification experiments were selected to be 850 °C, 900 °C and 950 °C. In each experimental run, the sample was heated at 50 K/min up to final gasification temperature in N_2 atmosphere. When the desired temperature was reached, N_2 was replaced by CO_2 with the flow rate of 100 ml/min. The final temperature was kept constant for 60 min (1hr) during gasification (isothermal gasification).

2.7. Data analysis

2.7.1. Char reactivity measurement in TGA

The weight loss of biomass was recorded against the reaction time in the system. The initial reaction time (t_0) was taken once CO_2 flow was supplied, and the corresponding weight of the sample was taken as the initial weight (W_0). The sample conversion X and reaction index R_s were calculated by following equations:

$$x = \frac{w_o - w_t}{w_o - w_f} \quad (3)$$

$$R_s = \frac{0.5}{\tau_{0.5}} \quad (4)$$

w_0 is the initial sample weight, while W_t is the sample weight at any gasification time t. W_t is the final weight and $\tau_{0.5}$ is the gasification time (min) for biomass when it reaches 50% conversion.

2.7.2. Gasification kinetic analysis

A number of kinetic models were employed for studying the isothermal gasification kinetics, which include volumetric model (VM), grain model (GM), random pore model (RPM) and modified volumetric model (MVM). VM, GM, and MVM were selected in this study, the volumetric model assumes that the reaction of biomass is in the same phase. While the grain model assumes that the non-porous grains shrink during the reaction. The MVM is the modified volumetric model. This kinetic equation is expressed as $\frac{dx}{dt} = k \cdot f(x)$, where:

$f(x)$ represents the change in char structure during gasification, k is the rate of reaction related to the unit of grain surface and $\frac{dx}{dt}$ can be measured experimentally from the TGA. VM and GM are shown in equation 5 and 6, respectively.

$$\frac{dx}{dt} = k_v(1 - X) \quad \text{or} \quad -\ln(1 - X) = k_v \cdot t \qquad (5)$$

$$\frac{dx}{dt} = k_s\,(1 - X)^{2/3} \quad \text{or} \quad 3(1 - X)^{1/3} = k_s \cdot t \qquad (6)$$

k_v and k_s denote the volumetric and surface reaction rate constants, respectively. Assuming char carbon dioxide is a first-order reaction, the gasification reaction kinetic parameters can be acquired from the Arrhenius equation.

3. Results and discussion

3.1. *Characterization of raw and pre-treated grass biomass*

Biomass characterization is imperative in evaluating the impact of the pre-treatment method on biomass fuel properties. As previously mentioned, when the biomass is pre-treated by torrefaction or leaching, biomass re-structuring is prompted, resulting in the liberation of moisture, volatiles and non-condensable gases [13]. Thus, the product from torrefaction or leaching becomes less recalcitrant with improved fuel properties [28].

The proximate and ultimate results for the raw and pre-treated grass are presented in Table 1. The ash content decreased in wet torrefaction. The decrease in the ash content of the biochar could be a result of the decomposition of the inorganic carbonates and oxides of minerals within the biomass into the liquid phase [36]. On the contrary in leaching and dry torrefaction there was an increase in ash content. The increase in ash content might be due to the breakdown of the above-mentioned inorganic carbonates and oxides, known as ash, from the minerals within the biomass. There was a decrease in volatile matter (VM) in all the three pre-treatment methods with the highest decrease being observed in dry torrefaction. The devolatilization process leads to the carbonization of the grass biomass and this is reflected by the increase in the fixed carbon content in all the three pre-treatment methods. The wet torrefaction method produced the highest increase in the fixed carbon content.

The results of the ultimate analysis showed that the hydrogen and oxygen content decreased in all the three pre-treatment methods. The highest decrease in hydrogen content was in the dry torrefaction method, while the highest decrease in oxygen content was in the wet torrefaction. The carbon content and the heating value increased in all the pre-treatment methods and the highest increase for both cases were in the wet torrefaction method. The nitrogen content decreased both in leaching and wet torrefaction methods but increased in dry torrefaction method.

Table 1. Characteristics of raw and pre-treated grass biomass

Samples	Proximate analysis (wt.%,db)			Ultimate analysis (wt.%, db)					CV (MJ/kg)
	Ash	VM	FC	C	H	O	N	S	
Raw	9.3	72.33	12.2	45.6	6.4	46.4	1.6	0	18.51
Leach	11.14	68.1	19.35	52.2	6.3	40	1.5	0	19.01
Dry torr	11.05	60.5	26.5	54.6	5.7	37.9	1.8	0	20.04
Wet torr	6.26	63.5	27.5	56.1	5.9	36.6	1.4	0	21.02

VM: Volatile matter; FC: Fixed carbon; CV: Calorific value (MJ/kg)

The compositional difference between the H/C and O/C ratio of the raw biomass utilized in this study was presented in the Van Krevelen diagram (Figure. 1). The plot indicates an improvement in the properties of pretreated biomass grass with wet and dry torrefaction having a higher reduction of H/C and O/C ratios than the leached hydrochar. The reduction in H/C and O/C ratios is a result of the dehydrogenation and the deoxygenation of the torrefied grass biomass and this leads to an increase in the reactivity of torrefied grass biomass [20]. Brigdeman et al.,[37] reported the carbon content increase of 7.4 % in the reed canary grass by dry torrefaction (250 °C). Wilk et al.,[38] evaluated the effect of hydrothermal carbonization (wet torrefaction), torrefaction and slow pyrolysis of Miscanthus giganteus (giant grass). They found wet torrefaction had a higher influence in the reduction of H/C and O/C ratios than dry torrefaction.

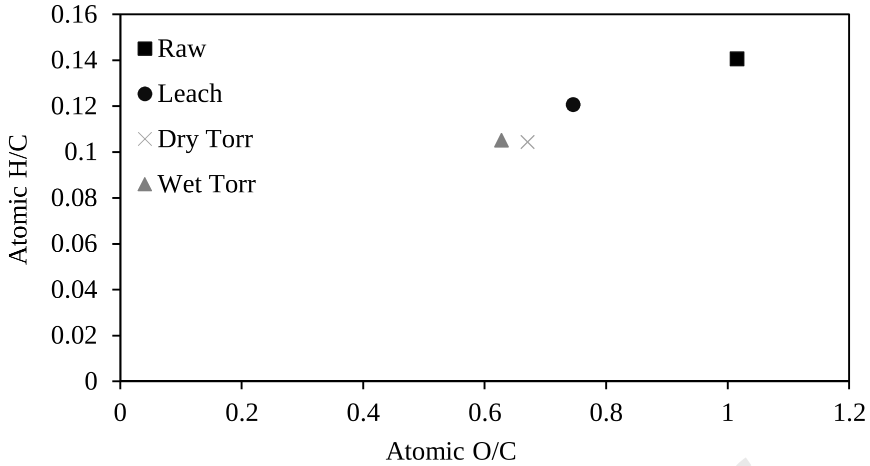

Fig. 1. Van Krevelen plot of raw and pre-treated grass

The inorganic constituents of the raw grass, leached grass char, dry torrefied char and wet torrefied hydrochar are presented in Figure 2. The results of the element analysis showed that pre-treatment, especially wet torrefaction and leaching process resulted in significant changes in the inorganic composition. Except for calcium, the concentrations of most inorganics such as Si, K, Mg, Fe, Cl and S decreased after both wet torrefaction and leaching. This trend was expected, since during wet torrefaction and leaching most of the inorganic species are broken down and released into the liquid phase. The filtration of the liquid from the solid hydrochar lead to the reduction in the concentration of the above-mentioned elements. The results further clearly showed that potassium was drastically reduced from 20.30 % to 1.50 % during wet torrefaction, while calcium increased from 18.88% to 37.40 %. A similar observation was reported by Bandara *et al.*, [29]. On the contrary the concentration of most the inorganic species increased during dry torrefaction and this is attributed to the fact that most of the inorganic minerals broken down are retained within the char produced.

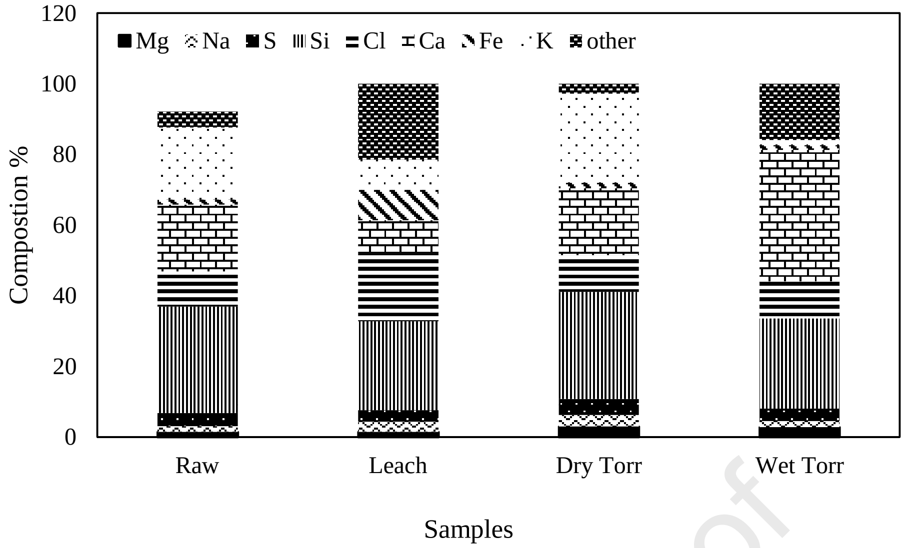

Fig. 2. Main elemental compositions in ash of raw and pre-treated grass

3.1.1. Mass yield and energy yield

Figure 3 shows the data for mass yield, energy yield, and energy density of raw and pre-treated grass. The pre-treatment of the grass has a notable effect on the mass yield and energy yield of char produced. The mass yield decreased to 98.50, 74.20 and 66.10 % for leached wet torrefied and dry torrefied char, respectively. This indicates that dry torrefaction and wet torrefaction have a higher effect on the mass yield than leaching based on the operating conditions. Dry torrefaction was carried out at 250 °C and wet torrefaction at 200 °C and leaching at 85 °C. At lower temperatures such as at the leaching temperature of 85 °C, most components of biomass namely hemicellulose, cellulose and lignin are not degraded. At 200 °C instead, thermal degradation occurs, and this leads to a higher weight loss and subsequently a decrease in mass yield. For energy yield similar results were obtained, the reduction in the energy yield was minimal in the leached sample (reduced from 100 % to 99.3 %), however wet torrefaction had the highest reduction (100 % to 75.8 %) and the dry torrefaction had an energy reduction from 100 % to 84.2 %). The reason for this could be due to the degree of thermal degradation of hemicellulose. Gong *et al.*,[28] reported that a higher degree of the thermal degradation of hemicellulose leads to an increase in the energy yield of the pre-treated biomass. When hemicellulose is degraded, there is a relative increase in the heat content of the remaining functional "lignin", as was observed in this study, with the lignin possessing a higher heating value (23-27MJ/kg) than hemicellulose with a heating value of 17-18MJ/kg [28]. In this study based on the mass yield value (66.1 %) achieved, dry torrefaction was found with a higher thermal degradation compared to wet torrefaction (74.2 %), hence this explains the difference in the energy yield for both methods. Wet torrefaction produced the highest energy density followed by dry torrefaction and lastly leaching correlating with the results obtained with the mass yield.

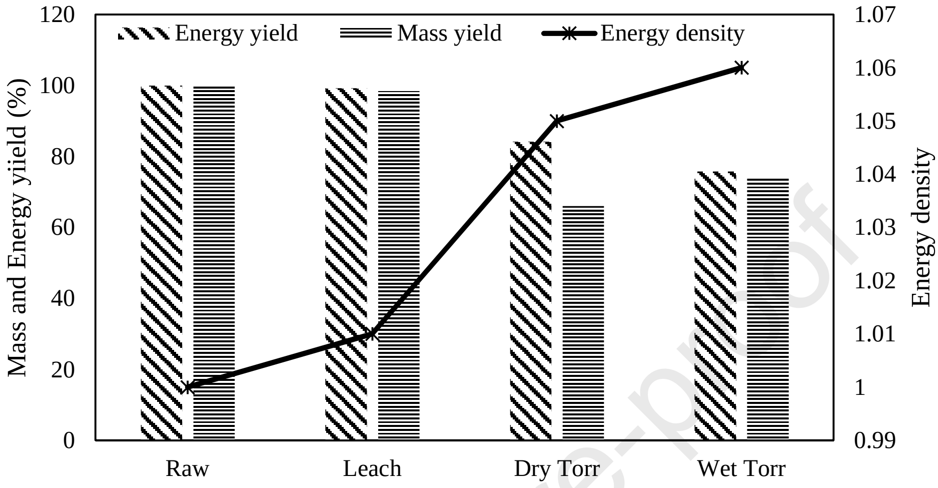

Fig. 3. Mass yield, energy yield, and energy density of raw grass and pre-treated grass

3.1.2 Morphological and structural characterization of raw and pre-treated grass biomass

Scanning electron microscopy (SEM) images of the raw grass and the pre-treated grass are represented in Fig. 4, to illustrate the impact of pre-treatment on grass morphology. From the images shown in Fig.4., it is noticed that all three pre-treatment methods lead to a change in the structure of the grass as a result of devolatilization, depolymerization, and carbonization reactions of hemicellulose, cellulose and lignin [29]. For raw grass sample a smooth surface and an unbroken fibre structure is observed. While, for wet torrefaction sample more pores and cracks are observed in the framework of the sample. An almost complete destruction of fibre and cracks is observed in a dry torrefied sample, mainly due to the increased devolatilization and depolymerization of biomass releasing volatiles and rearranging cellular structures. Similar results were reported by Li et al., [30] for torrefaction of bamboo at 250°C.

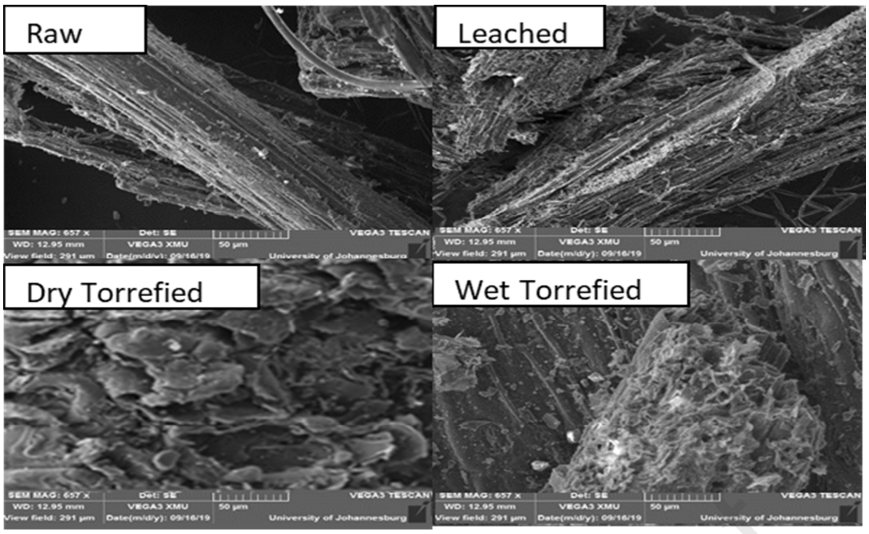

Fig. 4. SEM images of raw and pre-treated grass

3.1.3. BET of raw and pre-treated grass biomass

According to Chen *et al.*, [31] thermal treatment leads to an increase in pore volume and surface area. The specific surface area and pore structure distribution of raw and pre-treated biomass samples were assessed using Nitrogen (N_2) adsorption technique. Figure 5 shows the adsorption /desorption of raw and treated biomass. According to the International Union of Pure and Applied Chemistry (IUPAC) classification, all isotherms presented in Figure 5 displays a type II behaviour, which is a characteristic of micropores structure [32]. In all the samples, at a low relative pressure stage the curves rise gradually with the curved shape which indicates that adsorption process changes from monolayer to multilayer. For relative pressures higher than 0.8, all curves rise rapidly implying that medium and large pore structures also exist in all the biomass samples. Nonetheless, the presence of large pore structure is more visible in wet torrefied biomass sample.

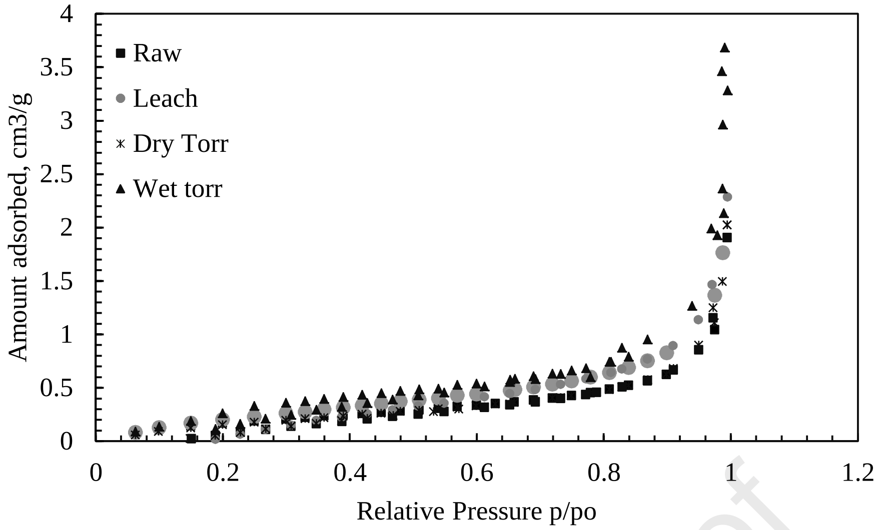

Fig. 5. Nitrogen adsorption isotherms obtained at -193 °C on raw and treated grass biomass

Table 2 shows the results of surface area and pore volume of raw and treated grass biomass. All the three pre-treatment methods increased both the surface area and pore volume. The surface area increased by almost a factor of 1.36 when the grass biomass was leached and increased by a factor of 1.14 when it was dry torrefied and by a factor of 70 in wet torrefaction. The pore volume increased by almost a factor of 1.20 when the grass biomass was leached and increased by a factor of 1.07 when it was dry torrefied and by a factor of 14.77 in wet torrefaction. Based on the above results wet torrefaction had the highest effect on the pore volume and surface area of the grass biomass.

Table 2 The BET results of raw and pre-treated grass

Samples	Surface area (m^2/g)	Pore volume (cm^3/g)
Raw	0.79	0.002945
Leach	1.08	0.003534
Dry Torr	0.90	0.003135
Wet Torr	1.81	0.043505

3.2. Effect of different pre-treatment methods on gasification properties of grass biomass

In order to clarify the impact of pre-treatment on CO_2 gasification of grass biomass, different pre-treatment methods i.e. torrefaction (dry and wet) and chemical leaching were applied and evaluated in terms of char conversion and reactivity. Figure 6 shows the char conversion vs time plots for different gasification temperatures of the raw and pre-treated grass biomass. The results showed that there was a reduction in the gasification time for all the three pre-treatment methods when compared to the raw biomass for all temperatures investigated (850-950 °C). The difference in the gasification time between torrefied grass biomass and raw biomass was more significant at 850, and 900 °C but less significant at 950 °C. This shows that the reactivity of pre-treated biomass when gasified at a lower temperature is more significant. Meaning that the increased reactivity as a result of pre-treatment is more significant when gasification is carried out at a lower temperature. Among the three pre-treatment methods studied, wet torrefaction has the highest char conversion rate at all temperature levels, followed by dry torrefaction and then leaching. This trend is linked to the increased pore size of the torrefied char which subsequently led to more active sites for conversion or reaction to take place. This effect of pre-treatment on biomass gasification was further verified by estimation of gasification reactivity values and presented in Fig.7.

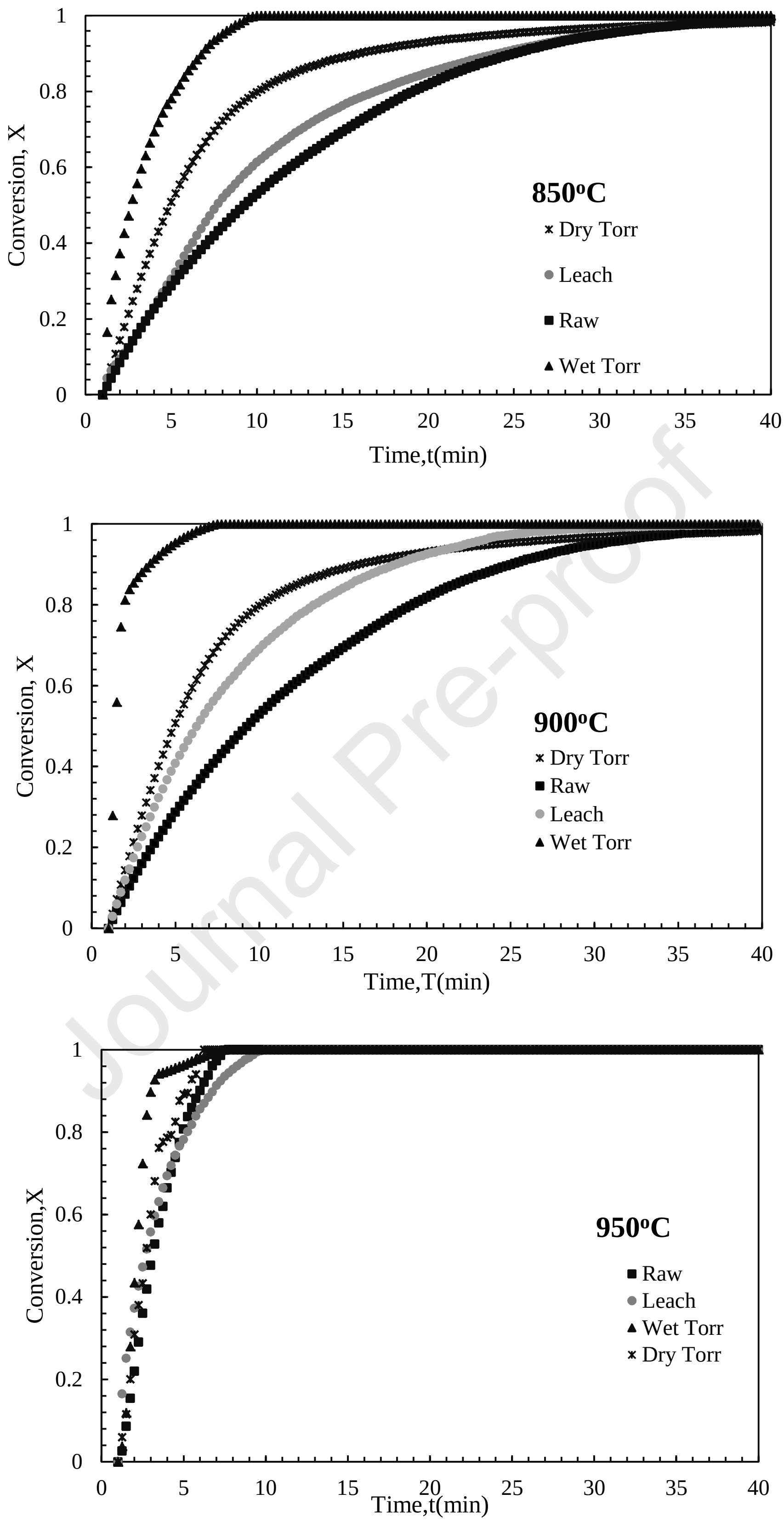

Fig. 6. Conversion vs time plot for raw and pre-treated grass at different gasification temperatures.

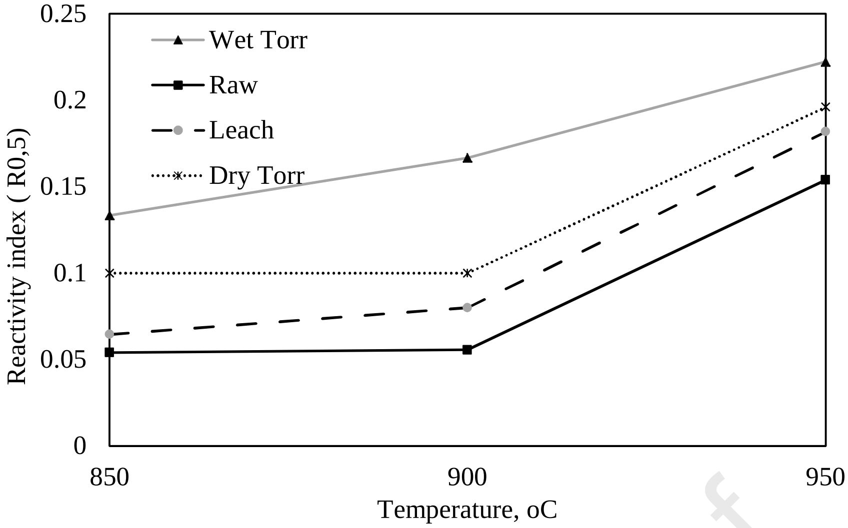

Fig. 7. Experimental reactivity of raw and treated grass biomass

The reactivity index is defined as 0.5 divided by the time required for the conversion degree to reach 50 %. Higher reactivity index therefore means higher reactivity. The reactivity index of wet torrefaction was much higher than the leached grass biomass. The reactivity index increased by almost a factor of 8 when the grass biomass was leached and increased by a factor of 26 when it was dry torrefied and by factor of 70 in wet torrefaction. The reactivity index also increased with the increase in temperature for all the samples, but the increase was more significant at higher temperatures of 950 °C. According to He *et al.*, [17] temperature rise stimulates the biomass molecules reactivity and the amount of active gasification area for reaction with CO_2, both of which improve the overall reactivity.

3.3. Kinetic modelling

The kinetics of raw and pre-treated biomass grass CO_2 gasification in the TGA system were studied. Figures 7-9 show the results from fitting the carbon conversion, X, and the reaction time, t, using the three reaction models of VM$-\ln(1-x)$, GM $(1-(1-x)^{1/3}$ and MVM $(lnx\ vs\ lnt)$ at different gasification temperatures (850-950 °C). The reaction rate constants, k, can be obtained from the slopes of the linearized relationships supplied by equation (5) and (6). The activation energy (Ea) for isothermal gasification was calculated from the slope of the $\ln(t)$ versus $\frac{1}{T}$, plots under a value of 0.9 % conversion (x). The square of correlation R^2 values, obtained from the three models for all the char samples are summarised in Table 3. For the model to be valid, the R^2 value should be close to 0.95. It was found that the three kinetics models performed well in most conditions. However, the highest coefficients R^2 of about of 0.99 for gasification of leached char at 900 °C indicated that VM and GM were the best suitable models for these experiments. Except for raw grass at 850 and 900 °C, the coefficients for gasification of the rest of samples was not very high for MVM but increased for GM and VM. From these results it could be concluded that the grain model was the best for describing the gasification kinetics of char samples in this study. These results are in agreement with the work done by Liu *et al*.,[39].

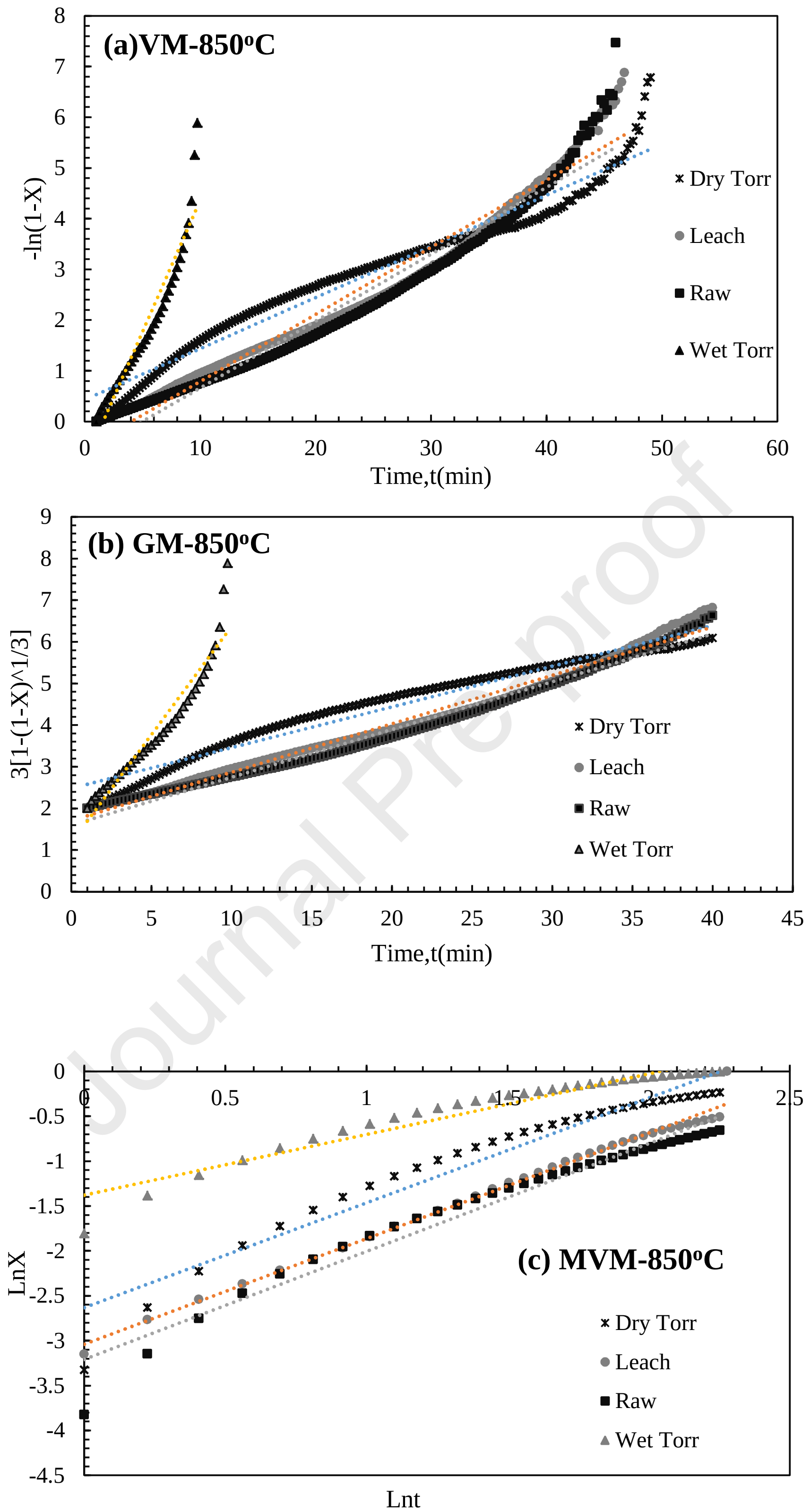

Fig. 8. The application of isothermal gasification kinetic models for raw and treated grass biomass at 850 °C.

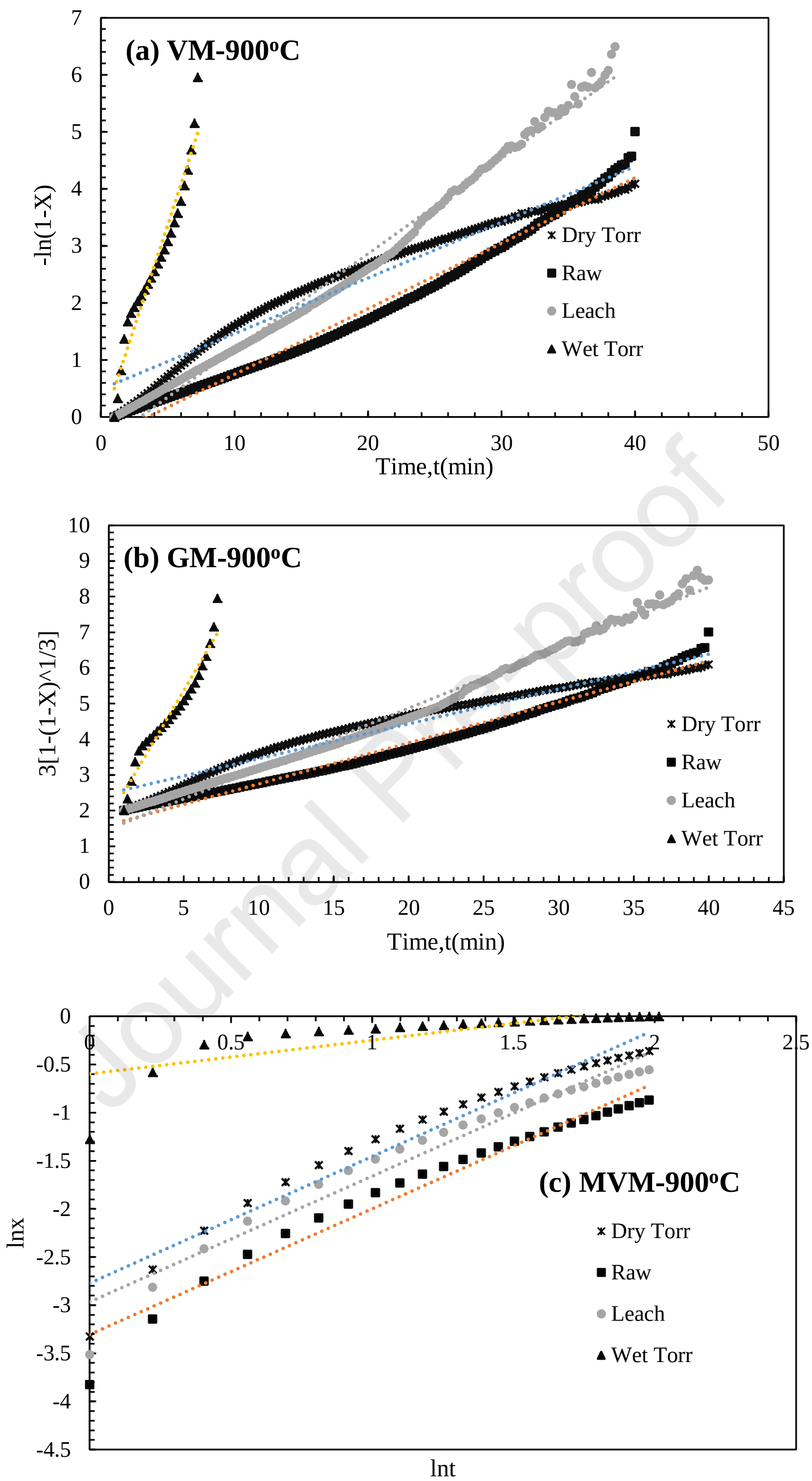

Fig. 9. The application of isothermal gasification kinetic models for raw and treated grass biomass at 900 °C.

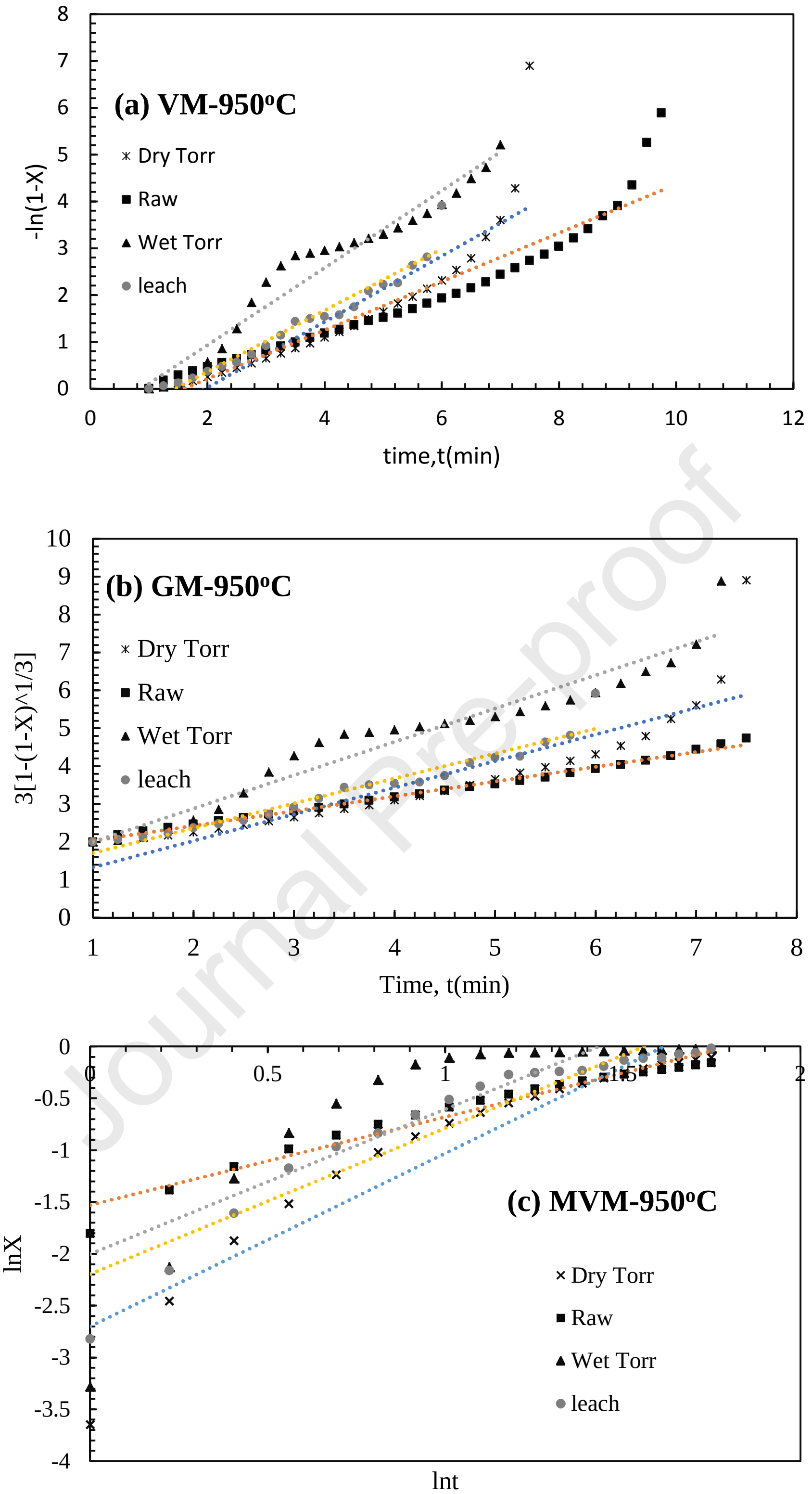

Fig. 10. The application of isothermal gasification kinetic models for raw and treated grass biomass at 950 °C.

Table 3. Kinetics model parameters.

Experiments	Temp (°C)	VM R^2	GM R^2	MVM R^2	E_a (kJ/mol)
Raw	850	0.9546	0.9843	0.9605	
	900	0.9827	0.9846	0.9619	161.71
	950	0.9758	0.9756	0.9301	
Leach	850	0.9659	0.9839	0.9895	
	900	0.9902	0.9905	0.9563	141.55
	950	0.970	0.9843	0.9573	
Dry Torr	850	0.9576	0.9571	0.9392	
	900	0.9571	0.9575	0.9539	124.33
	950	0.9422	0.9847	0.8973	
Wet Torr	850	0.9674	0.9779	0.9302	
	900	0.9548	0.9545	0.9563	86.97
	950	0.9468	0.9565	0.9153	

Fig. 11 shows the Arrhenius plots for raw and pre-treated grass biomass. The graphs clearly show a good linear relation between the lnt, and $1/T$, under different gasification temperatures (850, 900 and 950 °C). The activation energy (E_a) was obtained by the slope and intercept of the plot of $lnk\ vs\ 1/T$. The calculated (E_a) is presented in Table 3. The value of activation energy for raw grass (161.7073 kJ/mol) was greater than those of the pre-treated grass.

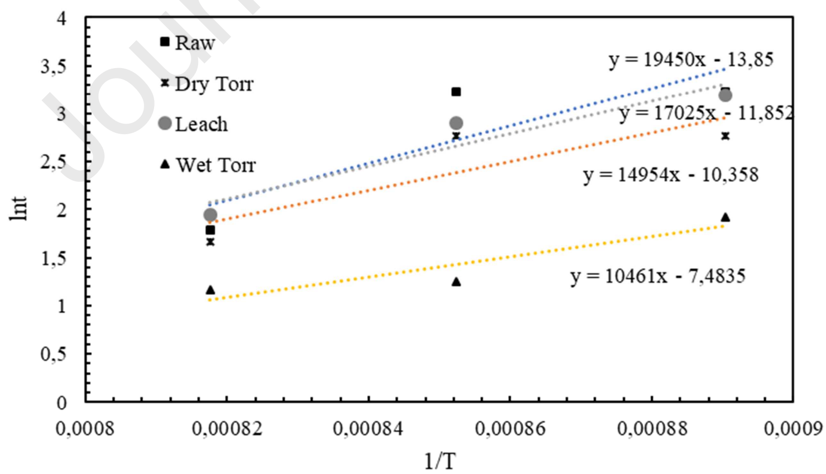

Fig. 11. Arrhenius plots for raw and pre-treated grass biomass

The effect of the different pre-treatments on activation energy showed that the activation energy of raw grass biomass was reduced from 161.7 kJ/mol to 141.5 kJ/mol for leached grass, 124.3 kJ/mol for dry torrefied and 86.9 kJ/mol for wet torrefied grass. This trend may be linked to the rate of reaction, hence as the reaction rate is increased the activation energy is reduced, $k = Ae^{-Ea/RT}$.

In this study there was a clear correlation between the char reactivity and the E_a hence it was observed that, chars with a higher reactivity exhibited a lower value of E_a . Based on the R^2 values GM has the best fit with the experimental results than the other two models (VM and MVM)

4. Conclusion

The effect of three different pre-treatment methods namely leaching, dry torrefaction and wet torrefaction on grass biomass properties such as energy density, calorific value and its effect on gasification efficiency were evaluated. The three pre-treatment methods all influenced the grass biomass properties and their gasification efficiency. Wet torrefaction had the most significant effect on the grass biomass properties such as carbon content, calorific value and energy density when compared to dry torrefaction or leaching. In terms of gasification efficiency, wet torrefaction reduced activation energy of raw grass biomass from 161.7 kJ/mol to 86.9 kJ/mol and dry torrefaction reduced the activation energy to 124.3 kJ/mol and leaching reduced the activation energy to 141.5 kJ/mol. Amongst the kinetic models studied to determine the gasification kinetics, grain model (GM) was the best suited for describing the biomass chars.

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6. Conflict of Interest

The authors declare that there is no conflict of interest in this research work

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Highlights

- Effects of different pretreatment methods on gasification properties of grass were evaluated
- The three pretreatment methods are dry torrefaction, wet torrefaction, and chemical leaching
- Wet torrefaction improved gasification properties more than dry torrefaction and leaching
- Wet torrefaction had the highest reactivity index of 0.25; dry torrefaction 0.18; leaching 0.16

Effect of different pre-treatment methods on gasification properties of grass biomass

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Abstract

The effect of different pre-treatments method on the gasification efficiency of grass biomass have not previously been evaluated. In this study, the effect of three different pre-treatment methods on gasification properties of grass biomass was investigated under CO_2 conditions. The pre-treatment methods were dry torrefaction, wet torrefaction, and leaching (chemical). The results obtained showed that the heating values increased by 2,77 % in the leached grass, 8,3 % in the dry torrefied grass and 13,5 % in the wet torrefied grass. However, the wet torrefaction had the highest reactivity index of 0,25 followed by dry torrefaction 0,182, then leaching 0,156. The effect of the different pre-treatment on activation energy showed that the activation energy of raw grass biomass was reduced from 161,7 KJ/mol to 141.5 KJ/mol for leached grass, 124.3 KJ/mol for dry torrefied and 86.97 KJ/mol for wet torrefied grass. These results show that wet torrefaction can improve gasification properties significantly when compared to dry torrefaction and leaching. The pore structure and pore volume effect of treated biomass was likely the predominant reason for the better char reactivity and conversion during gasification of wet torrefied sample. The research supplied an insight into the effect of different pre-treatment methods on grass biomass gasification

Keywords: Biomass, Gasification properties, Grass, Torrefaction, Leaching

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

On behalf of the other authors.

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