A Comparison Study on Original and Torrefied Hazelnut Shells using a Bubbling Fluidised Bed Gasifier

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Abstract

Torrefaction is mild thermo-chemical process similar to pyrolysis, that can be applied to biomass to improve energy density and hydrophobicity. Comparison was made between original and torrefied forms of hazelnut shell agricultural waste biomass, when these materials were subjected to gasification using a "bench-scale" fluidised bed gasifier. Results indicated that a simplified torrefaction process was successful in physical transformation of the hazelnut shell and that the resultant syn-gas was of a relatively higher calorific value, together with lower tar content.

Keywords: biomass, TGA, thermogravimetry, thermogravimetic analysis, gasification, fluidisation

1   Introduction

Gasification is a thermal conversion technique that occurs in an environment of insufficient oxygen, to prevent (more thermodynamically favourable) combustion. A significant advantage of gasification compared to combustion is the additional ability to generate a gaseous product which can be used for various chemical syntheses, compared to combustion (useful heat output only). Thus, gasification of hazelnut shell is an example biomass agricultural crop residue that can be used as a renewable source for chemicals and energy. Torrefaction is a mild pyrolysis process (thermal conversion in the *absence* of oxygen) to change certain thermo-chemical characteristics of biomass, notably to increase energy density and increase hydrophobicity which can improve physical distribution compatibility of biomass with coal. A "bench-scale" gasifier was used to compare the thermo-chemical characteristics of original and torrefied hazelnut shell, by measurement of certain parameters such as initial composition, syn-gas composition of major gas components and analysis of trace components via gas chromatography.

2   Methods

Hazelnut shell of average particle size $1\,\mathrm{mm}$ was converted to syn-gas using a "bench-scale" gasifier (Figure 1), which operates at atmospheric pressure and achieves fluidisation velocity $0.28\,\mathrm{m\,s^{-1}}$. In addition, the gasification zone length (from the fluidised bed surface) is $0.5\,\mathrm{m}$ and residence time of the fuel in the gasifier is $1.81\,\mathrm{s}$.

The biomass was stored in a fuel hopper and two Archimedes helix screw feed tubes were used to transfer fuel into the gasifier. The feeding rates are controlled via the motors with variable speed drive system to rotate these

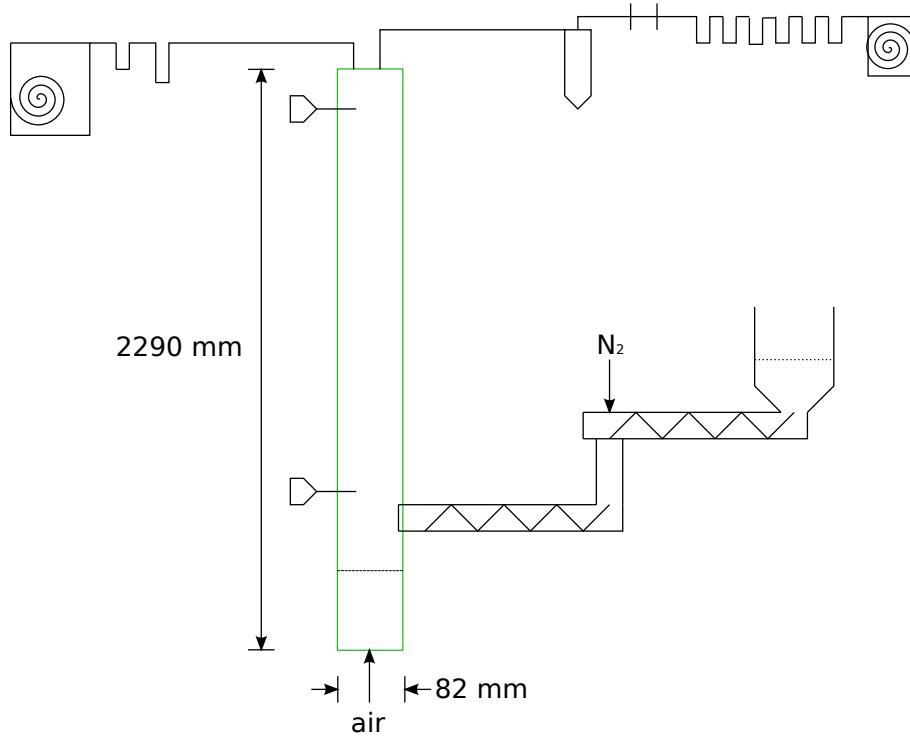---

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Figure 1: Diagram of bench-scale gasifier

helix screw tubes. There is a supply of nitrogen gas in the feeding system to facilitate the transfer of the fuel. The fluidisation distributor plate comprises a series of four concentric rings of holes each of diameter about 0.5 mm and spatial distance 4 mm between each hole; the distance between each concentric line of holes is approximately 10 mm. The gasifier system was pre-heated using electrical trace heating filaments to a temperature of 800 C, to maintain the allothermal gasification conditions.

After reaching the gasification temperature under nitrogen flow, fuel and air feeding started and combustion conditions were established. Gasification was reached by a sequential, stepwise decrease of the air to fuel ratio. During the transition from the combustion to gasification regime, the gaseous product streams were analysed in real time, "online". When the gasification conditions were established, the output syngas composition was considered to be stable after 30 minutes duration. Then, the test run started at the target equivalence ratio.

The syn-gas composition was measured to determine the "initial" condition of the gasifier, using process gas chromatography analyser and repeated after an additional 60 minutes operation of the gasifier, at which time the gasifier was considered to be operating at a "stable" condition. The final feedstock, air and nitrogen flow rates at stable condition were used for the determination of the operating parameters such as equivalence ratio.

At stable gasification regime, gas samples were collected through sulfinert pipe fittings, using polyvinyl fluoride (Tedlar) sample bags for subsequent analysis using gas chromatography. At the end of each gasification test (approximate total duration 90 minutes at stable conditions), a "sample train" of condensed tars was collected for further analysis using gas chromatography. Ash from both the fludized bed base (bottom ash) and flue gas outlet (fly ash) were collected and chemical analysis was performed by Inductively Coupled Plasma spectroscopy (ICP).

This experimental test was repeated on a separate torrefied hazelnut shell sample which was gasified at the same conditions with the original feedstock. Torrefaction of hazelnut shell was performed using a furnace oven. Torrefaction was expected to alter the physical characteristics of the hazelnut shell and therefore, the effect of torrefaction was confirmed by development of a simple hydrophocity test as given below:

1. 1 gram of torrefied biomass sample measured and 2 ml of tap water added. This was repeated for an additional 4 torrefied biomass samples

2. step 1 repeated with 5 non-torrefied, original biomass samples.

3. Samples left at original ambient laboratory conditions, for 60 minutes.

4. Each sample was transferred onto cellulose filter paper and the biomass spread over the filter paper area until the depth of biomass on the filter paper is equivalent to the particles' sizes.

5. Samples were left to dry at original ambient laboratory conditions, for 30 minutes.

6. Masses of the samples were measured using an analytical balance.

3   Results

3.1   Torrefaction

Due the thermal mass effects of the oven and the steel box container used to hold the biomass sample, various iterations (Table 1) of torrefaction were performed with a general limit of maximum temperature 300 C and heating rate less than $1\,C\,s^{-1}$. The extent of torrefaction was evaluated using a simple hydrophobicity test as mentioned above torrefed samples were compared to original hazelnut shell.

Therefore, with respect to sample 1, temperature was increased from 30 C to 290 C at a heating rate of 0.9 C/sec (54 C/min), then held at 290 C for 600 sec. Visual inspection of the samples was made and determined that torrefaction was incomplete. The oven was allowed to cool naturally to 110 C, then a new temperature program applied to increase the temperature to 270 C (heating rate 0.9 C/sec). The sample was then held at that temperature for 360 sec. Visual inspection was repeated until torrefaction considered incomplete, therefore the subsequent iterations were made).

Table 1: Torrefaction iterations

	Sample 1	Sample 2
Mass (kg)	1.7	2.5
Initial programme (C)	30–290	20–290
Initial temperature rate $(\mathrm{C\,s^{-1}})$	0.9	0.9
Maximum temperature duration (seconds), initial	600	1200
Iteration 1 (C)	110–270	254–280
Temperature rate, iteration 1 $(\mathrm{C\,s^{-1}})$	0.9	—
Maximum temperature duration (seconds), iteration 1	360	240
Iteration 2 (C)	160–280	279–280
Temperature rate, iteration 2 $(\mathrm{C\,s^{-1}})$	1	—
Maximum temperature duration (seconds), iteration 2	240	480
Iteration 3 (C)	—	238–280
Temperature rate, iteration 3 $(\mathrm{C\,s^{-1}})$	—	—
Maximum temperature duration (seconds), iteration 3	—	1200
Iteration 4 (C)	—	262–280
Temperature rate, iteration 4 $(\mathrm{C\,s^{-1}})$	—	—
Maximum temperature duration (seconds), iteration 4	—	480

Where temperature increase rates are omitted in Table Table 1 (e.g. iteration 1, sample 2), this indicates that the programmable temperature increase rate function was not used. The oven door was opened prior to each iteration, to inspect the torrefaction process. If torrefaction was considered incomplete and the temperature of the oven relatively high, the iteration was performed without a temperature increase rate. Therefore, for iteration 1, sample 2, the lower value of the temperature range indicates the temperature at which the oven door was closed and the iteration started. Determination of torrefaction was a subjective process, initially by visual inspection of the sample biomass material; the following photograph (Figure 2) shows the difference in appearance between original and torrefied hazelnut shell. Hydrophobicity tests were subsequently performed, to confirm the success of the torrefaction process.

3.2 Biomass composition

Samples of hazelnut shell were analysed for chemical composition in accordance with extant standards (e.g. ASTM D 5373-14, shown in Table 2).

3.3 Thermo-gravimetric analysis

An indication of the effect of a torrefaction process on a biomass sample can be seen via thermo-gravimetric analysis (TGA, Figure 3). To represent an ideal torrefaction process, a TGA program of temperature increase rate 55C min $^{-1}$ maximum temperature 300 C. This is analogous to typical application of mild pyrolysis conditions [3]:

- heating rate $< 1\mathrm{C\,s^{-1}}$

- maximum temperature $300\,\mathrm{C}$

Figure 2: Photograph of original and torrefied hazelnut shell

Table 2: Ultimate analysis of hazelnut shell (% weight values shown, original "as received" basis)

	original	torrefied
C	47.98	53.71
H	6.30	5.92
N	0.46	0.40
S	0.06	0.01
O	33.63	35.96
Water	10.44	2.96
Ash	1.13	1.04

For comparison, TGA thermograms were also measured for original and torrefied hazelnut shells (Figure 4), using a temperature programme of temperature increase rate $15\,\mathrm{C\,min^{-1}}$ and maximum temperature $1000\,\mathrm{C}$.
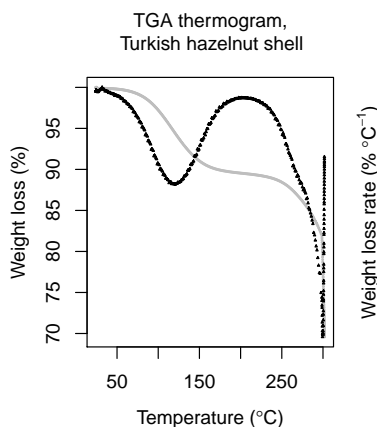

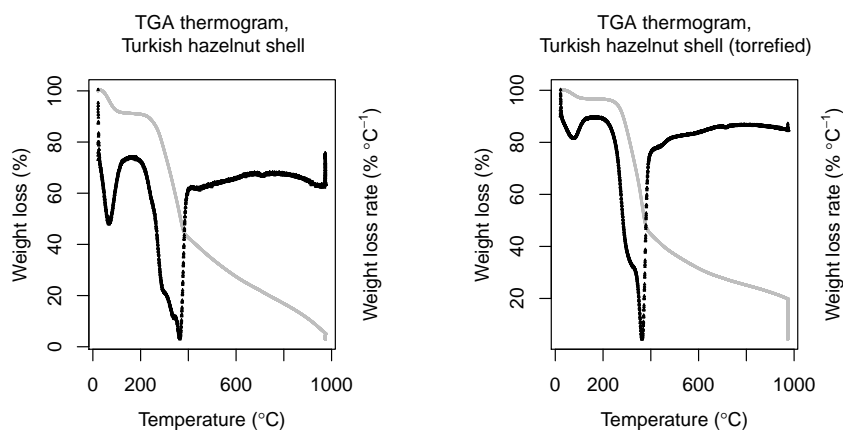Figure 3: TGA of representative ideal torrefaction process (weight loss indicated by grey line)

Figure 4: TGA of original and torrefied hazelnut shell (weight loss indicated by grey line)

3.4 Hydrophobicity

Hydrophobicity is an indication of water retention by a sample and was measured by the following procedure, a simplified adaptation of various methods summarised elsewhere [10]; changes in masses of dry and water-immersed samples were then calculated as percentage values (Figure 5):

3.5 Gasifier operation

Gasification of the biomass fuels produced a *syn-gas* of a composition summarised in the following table for the gasifier used in this project (Table 3):

**Difference in hydrophobicity,
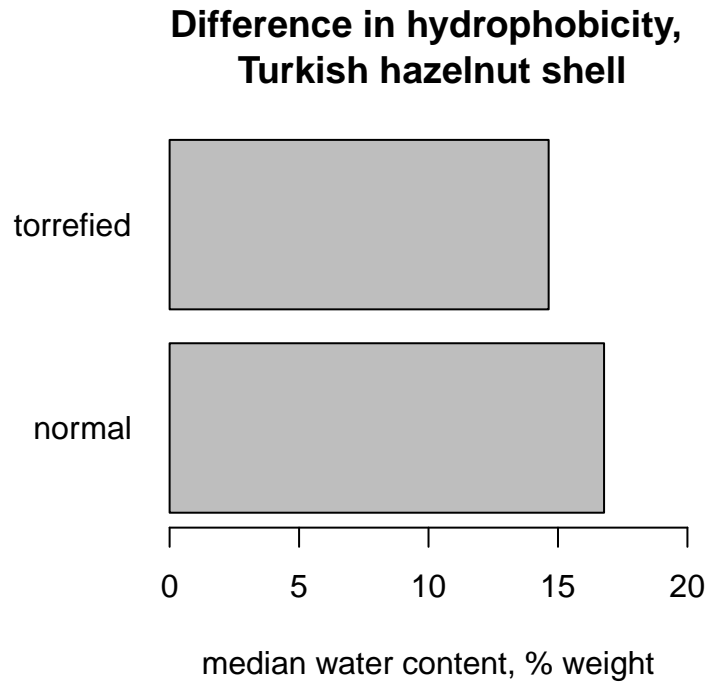Turkish hazelnut shell**

Figure 5: Graph to show difference in water retention between original and torrefied hazelnut shell

Table 3: Syn-gas composition from the gasifier using original and torrefied hazelnut shell fuels (values expressed as % volume basis)

	original	torrefied
N_2	55.21	52.51
CO	15.75	17.39
CO_2	14.58	15.42
CH_4	5.77	5.71
H_2	8.69	8.97

3.6   Surface analysis

A Scanning Electron Microscope (SEM) was used to investigate if the torrefaction process causes a visible change in the hazelnut shell surface (Figure 6), i.e. a change in porosity.
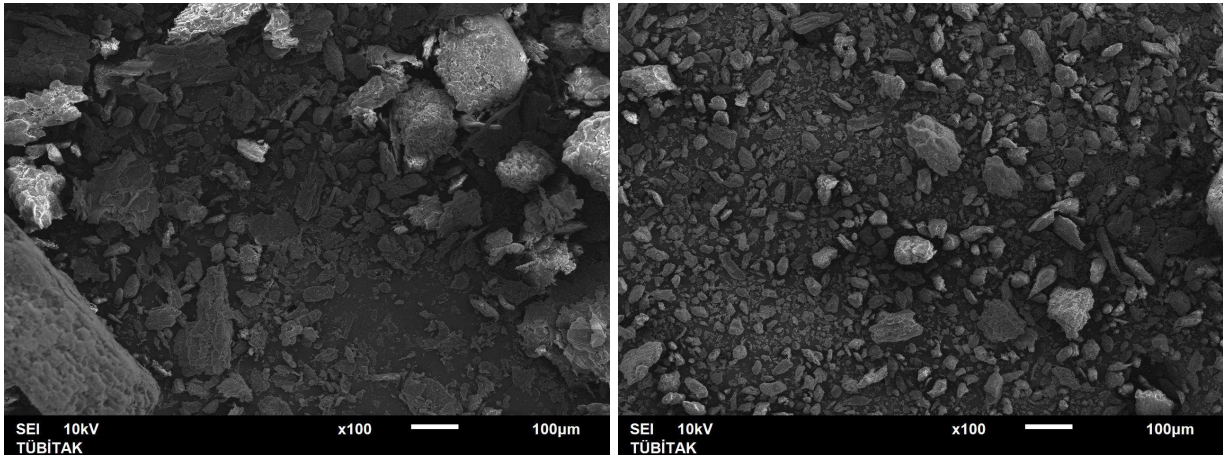

Figure 6: SEM images of original and torrefied hazelnut shell

3.7   Tar analysis

With reference to biomass thermal conversion, tars are defined generally as hydrocarbons that may condense from the gaseous phase as they enter relatively cooler zones of a gasifier, away from the main gasification zone. A range of tars were detected by GC as shown in (Figure 7), from which total concentrations of tars were found to be $36\,\mathrm{g\,C\,m^{-3}}$ and $30\,\mathrm{g\,C\,m^{-3}}$ for original and torrefied hazelnut shell samples respectively.

3.8   Sulphur analysis

Sulphur content — in gaseous form — was detected using gas chromatography and quantified as shown in Table 4. In addition, total sulphur content of collected tar samples in isopropanol was also measured with both pulsed flame photometric detector (PFPD) gas chromatography and UV fluorescence detector; found to be $1.6\,\mathrm{mg\,S\,l^{-1}}$ and $1.36\,\mathrm{mg\,S\,l^{-1}}$, for original and torrefied hazelnut shell samples respectively.

Table 4: Gaseous form sulphur, collected from flue gas sample bags (ppm, mole basis)

	original	torrefied
H_2S	48.6	42.6
COS	6.5	5
Total S	37.37	32.9

3.9   Ash analysis

The hazelnut shell ash was subjected to inorganic analysis (Table 5) and in addition, a comparison between the extent of non-oxidised carbon was also made (Table 6).

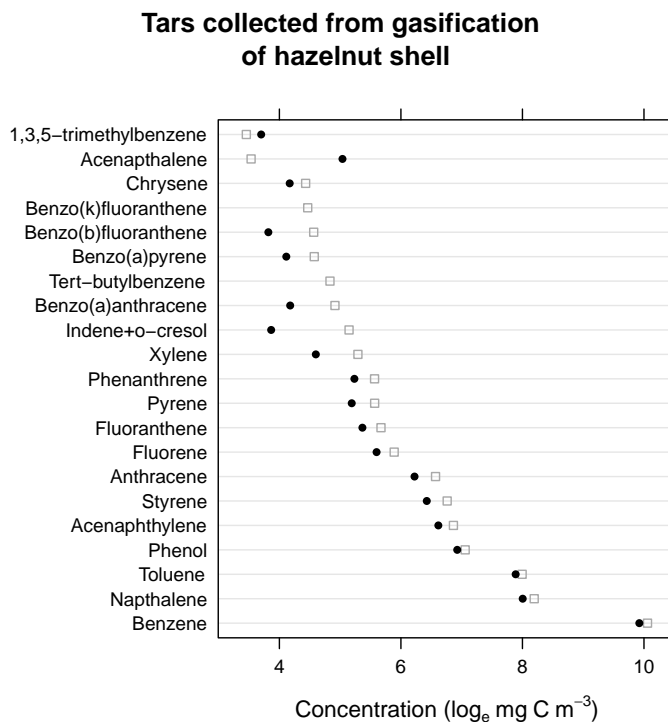**Tars collected from gasification
of hazelnut shell**

Figure 7: Range of tars detected, gasification of hazelnut shell original (indicated by square symbol □) and hazelnut shell torrefied (indicated by solid circle symbol •)

Table 5: Ash analysis of hazelnut shell (total ash $1.26\,\%$ weight fuel, dry)

Element	weight $(\mathrm{mg\,kg,}^{-1}$ fuel, dry)	Compound/ compound	weight $(\mathrm{mg\,kg,}^{-1}$ fuel, dry)
Al	78.16	Al_2O_3	147.72
Ca	1339.88	CaO	1875.84
Fe	111.66	Fe_2O_3	159.67
K	1228.23	K_2O	1473.87
Mg	200.98	MgO	333.63
Mn	44.66	MnO	57.61
Na	111.66	Na_2O	150.74
P	111.66	P_2O_5	255.69
Si	178.65	SiO_2	382.31
Zn	100.49	ZnO	124.61

Table 6: Unburnt carbon in ash samples (% weight basis)

	original	torrefied
Gasifier bottom ash	69.96	94.31
Cyclone fly ash	19.86	49.69

4   Discussion

Ideal conditions for the torrefaction process is an inert atmosphere that does not contain oxygen. This could not be achieved with the apparatus available, but the use of a stationary container (as opposed to a dynamic rotary container with a continual flow of inert gas) appears to be satisfactory. Comparison of the chemical compositions of both original and torrefied hazelnut shell show that the experimental procedure conducted in this article achieved the objectives of the torrefaction process: an increase in carbon for improved energy density (Table 2); an increase in hydrophobicity (as indicated in Figure 5). Change in hydrophobicity may be associated with alteration in the porosity of the biomass particles due to the torrefaction process. Use of SEM analysis indicates that the fibrous characteristic of original, or raw, biomass is reduced by the torrefaction process, which in addition to a change in porosity also improves fluidisation [5]. The measurement of hydrophobicity is open to subjective interpretation, which could be improved by the development of a common standard test, similar to those extant for other characteristics such as moisture content or elemental analysis.

Ash composition analysis (Table 5) is consistent with previous observations whereby hazelnut shell ash is also measured and found to be relatively low (1.2 % weight dry) compared to other biomass types (e.g. wheat straw, 7.2 %) [2] and furthermore, the difference between unburnt carbon in the ash residues (Table 6) suggests that the higher carbon content of torrefied fuel is responsible for this observation. Similarly, the quantity of sulphur detected in the tar condensates decreases from the original to the torrefied samples by 15 % and total gaseous form sulphur decreases by approximately 12 %. This suggests that sulphur is lost as volatile compounds during the torrefaction process, perhaps as found in previous studies [8] via decomposition of organic sulphur components in the biomass protein structure during pyrolysis at 200–300 C. Total tar emitted by torrefied hazelnut shell is also approximately 15 % less than original form hazelnut shell. Biomass combustion studies [4] have shown that napthalene is an important intermediate for formation of higher molecular weight poly-cyclic aromatic hydrocarbons (PAHs). Similar observations of the importance of napthalene have been documented elsewhere, concerning both pyrolysis of waste tyres [9] and biomass gasification [1]. In a review of preceding work [7], napthalene is the main pre-cursor to soot formation, with benzene and toluene involved in tar decomposition reactions; these three compounds were also the most prevalent compounds detected in measurement of tar for this study.

5   Conclusions

Hazelnut shell is waste residue material from a significant agricultural crop in Turkey. Torrefaction of this biomass resource was found to increase the hydrophobicity and thus improve manual handling compatibility with coal, initially for co-firing power generation in order to reduce fossil fuel pollution and subsequently for future development of gasification power generation. In addition to hydrophobic transformation of the biomass feedstock, syn-gas composition is also affected by the torrefaction process; increased carbon monoxide content and lower tar content were observed. Therefore torrefied biomass is a potential route to improved syn-gas quality, with respect to higher calorific value and lower tar content compared to original form biomass.

6 Acknowledgements

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7 Additional Files

Thermogravimetric data sets [6] are provided as "Open data" for use by other researchers.