

## Food and market waste – a pathway to sustainable fuels and waste valorization

Ouadi, Miloud; Bashir, Muhammad; Galileu Speranza, Lais; Jahangiri, Hessam; Hornung, Andreas

DOI:

[10.1021/acs.energyfuels.9b01650](https://doi.org/10.1021/acs.energyfuels.9b01650)

License:

Creative Commons: Attribution (CC BY)

*Document Version*

Publisher's PDF, also known as Version of record

*Citation for published version (Harvard):*

Ouadi, M, Bashir, M, Galileu Speranza, L, Jahangiri, H & Hornung, A 2019, 'Food and market waste – a pathway to sustainable fuels and waste valorization', *Energy & Fuels*, vol. 33, no. 10, pp. 9843-9850.  
<https://doi.org/10.1021/acs.energyfuels.9b01650>

[Link to publication on Research at Birmingham portal](#)

### General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

### Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact [UBIRA@lists.bham.ac.uk](mailto:UBIRA@lists.bham.ac.uk) providing details and we will remove access to the work immediately and investigate.



# Food and Market Waste—A Pathway to Sustainable Fuels and Waste Valorization

Miloud Ouadi,<sup>†</sup> Muhammad Asif Bashir,<sup>†</sup> Lais Galileu Speranza,<sup>†</sup> Hessam Jahangiri,<sup>\*,†</sup> and Andreas Hornung<sup>†,‡,§</sup>

<sup>†</sup>School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.

<sup>‡</sup>Fraunhofer UMSICHT, Fraunhofer Institute for Environmental, Safety and Energy Technology, An der Maxhütte 1, 92237 Sulzbach-Rosenberg, Germany

<sup>§</sup>Friedrich-Alexander University Erlangen-Nuremberg, Schlossplatz 4, 91054 Erlangen, Germany

**ABSTRACT:** Food and market waste (FMW) is one of the most abundant unrecycled products which poses waste management issues and negative environmental impacts. Thermo-catalytic reforming (TCR) is a pyrolysis based technology which can convert a wide range of biomass wastes into energy vectors bio-oil, syngas, and char. This paper investigates the conversion potential of FMW into sustainable biofuels. The FMW was processed using a laboratory scale 2 kg/h TCR reactor. The process produced 7 wt % organic bio-oil, 53 wt % permanent gas, and 22 wt % char. The bio-oil higher heating value (HHV) was found to be 36.72 MJ/kg, comparable to biodiesel, and contained a low oxygen content (<5%) due to cracking of higher molecular weight organics. Naphthalene was detected to be the most abundant aromatic compound within the oil, with relative abundance of 12.95% measured by GC-MS. The total acid number of the oil (TAN) and viscosity were 11.7 mg KOH/g and 6.3 cSt, respectively. The gross calorific value of the produced biochar was 23.64 MJ/kg, while the permanent gas showed a higher heating value of approximately 17 MJ/Nm<sup>3</sup>. Methane (CH<sub>4</sub>) was found to be the largest fraction in the permanent gases reaching over 23%. This resulted either due to the partial methanation of biosyngas over the catalytically active FMW biochar or the hydrogenation of coke deposited on the biochar in the post reforming stage.

## 1. INTRODUCTION

Concerns over security and energy demand, together with the impact of CO<sub>2</sub> emissions from fossil fuel usage, contributing toward climate change are driving the need to find sustainable and alternative energy sources.<sup>1,2</sup>

Biofuels are considered to be one of the most efficient routes for reducing transportation carbon emissions and dependence on fossil fuels.<sup>3</sup> Among the many possibilities for biofuel production and supply, fuels from food waste can counteract the accumulation of unrecycled product from various food industries; thus addressing two environmental impacts concurrently.<sup>4,5</sup> Food waste originates from various segments of the food supply chain. It includes generation from the food production industry (postharvest residuals such as fruit and vegetable residuals); food processing and packaging (wastes from breweries, slaughterhouses, vegetable peels, etc.); distribution and marketing (supermarket expired food, etc.), and the consumption sector (kitchen waste, meal leftovers, etc.).<sup>6</sup>

According to a report from the Intergovernmental Panel on Climate Change (IPCC), a large fraction (45%) of the total municipal solid waste (MSW) collected in Europe is food waste.<sup>7</sup> According to the estimation of the FAO (Food and Agricultural Organization), approximately 1.3 billion tons of food is wasted every year which is about one-third of the food produced globally.<sup>8</sup> In the United States (US), the average annual food waste feedstock resource estimates around 14 million tons.<sup>9</sup> Although, substantial measures have been taken to cut down the magnitude of food waste; it is still predicted to rise by 1.1 million tons by 2025.<sup>10</sup>

Food waste is a global problem which poses detrimental economic, social, and environmental impacts. UK food waste is a heavy source of global greenhouse gas emissions (GHG) of over 20 million tons, of which three-quarters arise in the UK. In developed countries, it is a serious matter for which sustainable methods for waste management have been legislated. In the UK, the food waste hierarchy has been defined to prevent and minimize its impact.<sup>11</sup>

On the other hand, despite posing disposal and environmental challenges, food waste can prove to be a sustainable source of energy. Food and market waste has attracted a lot of attention due to its rich organic composition. It has an energy content which can be converted into value-added products such as biochemicals, materials, enzymes, and biofuels. Valorization of food waste into biofuel is in greater demand than its conversion to chemicals.<sup>8</sup>

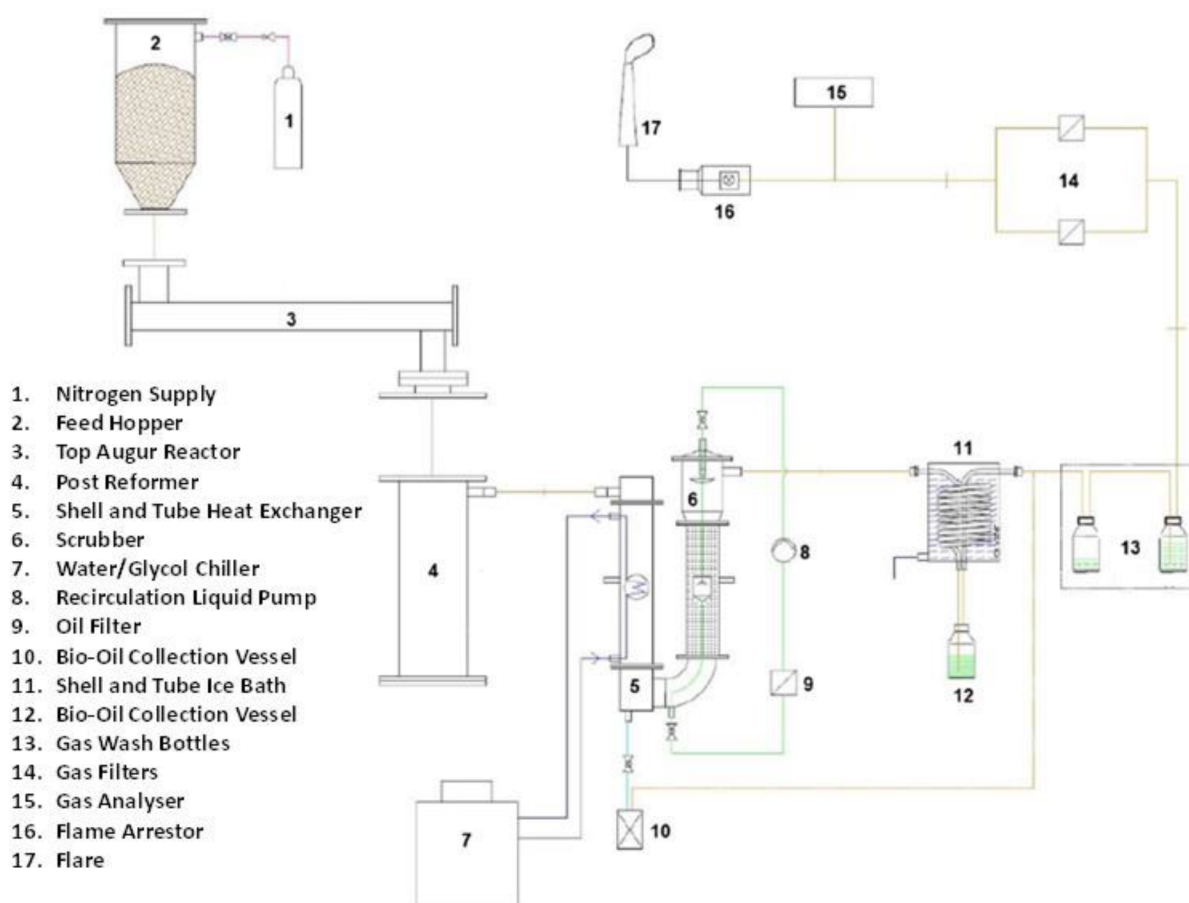
The methods prevalent for food waste disposal are landfilling, incineration, composting, and anaerobic digestion (AD). Landfilling is the most unwanted method that leads to significant emissions of methane, odor, and landfill leachate (liquid); all of which cause social, environmental, and health problems. Incineration is an old management technique to dispose of solid wastes which can reduce substantial volumes (80–85%) of solid waste by combustion. Furthermore, incineration generates heat which is used for energy purposes in the process industry. However, if uncontrolled combustion

Received: May 29, 2019

Revised: August 30, 2019

Published: September 11, 2019





**Figure 1.** Process path flow diagram (PFD) of the TCR (2 kg/h) plant.

can lead to higher carbon emissions than advanced thermal conversion processes (gasification and pyrolysis).<sup>8</sup>

Composting and anaerobic digestion are the two popular waste treatment methods which keep food waste out of landfills. Both methods work by biological degradation of the organic matter. Composting occurs in aerobic conditions and produces compost as the final product.<sup>7</sup> Composting is popular because it produces a fertilizer for soil treatment. However, this technique also comes with shortcomings such as the release of leachate,  $\text{NH}_3$ , greenhouse gases, odor, etc.<sup>12</sup> AD turns biomass into biogas and digestate in a controlled anaerobic atmosphere. The resultant biogas is a high source of energy with 60–70% methane along with  $\text{CO}_2$  (30–40%) and other traces, while the nutrient-rich digestate can act as a soil enhancer (fertilizer). Although, AD is an established waste management method for sewage sludge, wastewater, animal manure, but anaerobic digestion of food waste has caused some operational demerits. Low methane yield, process instability due to accumulation of volatile free fatty acids (FFAs); digester foaming due to high protein and lipid contents; and low buffer capacity owing of rapid digestion of volatile fatty-acids.<sup>6</sup> Furthermore, in some regions where land spreading of digestate waste is prevalent, soils can become over saturated with nutrients. Certain regions in Europe have now prohibited further land spreading of digestate in order to control nutrient concentrations entering the soil, this leads to farmers transporting digestate over longer distances for disposal.<sup>13</sup> To address these aforementioned issues, a sustainable and productive method is needed.

Production of bio-oil by intermediate pyrolysis,<sup>14,15</sup> fast pyrolysis,<sup>16,17</sup> hydrothermal liquefaction,<sup>18</sup> or gasification<sup>19</sup> and subsequent Fischer–Tropsch synthesis<sup>20</sup> are the main thermochemical technologies to convert wastes or biomass into liquid hydrocarbons. Thermo-catalytic reforming (TCR) is a new technology which is a combination of intermediate pyrolysis and postcatalytic reforming. This process contains two essential steps: (1) intermediate pyrolysis where the thermal heating and degradation of biomass occurs under the complete absence of oxygen, at intermediate heating rates and solid residence times (minutes) and (2) the reforming stage where the catalytic cracking of vapors occurs at elevated temperatures to promote the formation of synthesis gas and organic vapors, which when condensed, yield deoxygenated bio-oils with superior physical and chemical fuel properties.<sup>21,22</sup> The TCR is capable to produce  $\text{H}_2$  rich syngas, low oxygenated liquid fuel, and high energy dense char. The  $\text{H}_2$  rich syngas is an attractive option for combined heat and power (CHP) applications or  $\text{H}_2$  separation for use in fuel cells; the bio-oil can be used directly in stationary engines and heavy duty machinery or further upgraded to transport fuels; and the char can be applied as a soil enhancer or as a feedstock for combustors and/or gasifiers to generate energy.

The objective of this work was to investigate the sustainable biofuel potential of food and market waste via thermo-catalytic reforming. The TCR derived bio-oil, syngas and char were studied for their physical and chemical characteristics to determine their viability to be used as renewable fuels.

## 2. MATERIALS AND METHODS

**2.1. Raw Material.** Food and market waste (FMW) was collected from canteens, restaurants, fast-food restaurants, hotels, etc. (industrial gastronomy sector) as well as supermarkets (e.g., packed food) by a waste logistics company (Betz Entsorgung GmbH & Co) in Germany. About 230 kg FMW was received by the University of Birmingham and subsequently preconditioned (dried and pelletized) before thermal conversion. Due to the heterogeneous nature of FMW, this feedstock is highly variable in composition. Therefore, it must be noted that processing of this type of waste is highly dependent on the type of pretreatment involved and the scale at which it is processed. The results obtained from this study are not necessarily fully representative of FMW in general or from FMW obtained from different sources. As received FMW was in a slurry state containing over 80% moisture content. Due to excessive water in its raw state, it was mandatory to condition it by tray drying and pelletization prior to thermo-chemical processing. The raw FMW was dried using a Memmert UF750 oven at 80 °C for 4 h in multiple batches of no more than 10 kg each. The dried FMW reached a final average moisture content of 13 wt % and was shredded with HECHT-6420 garden shredder and pelletized using DORN-TEC PTE 50 pelletizer. All three prerequisites for the TCR processing were fulfilled on site. The final pellets were approximately 1.5 cm long and 0.7 cm mean diameter.

**2.2. Experimental Setup.** FMW was processed through a pilot scale TCR system (2 kg/h) located in Fraunhofer UMSICHT, Germany.<sup>23</sup> The system consists of a feed tank with 7 L capacity, two reactors (auger and postreformer connected to each other in series), and a cooling and gas filtration system. The process path flow diagram of the TCR system is shown in Figure 1. The first reactor being the intermediate reactor was operated at 450 °C, while the second reactor being a reformer operated at a high temperature of 700 °C. The total reactor length was 1000 mm which transferred the feedstock by means of an auger (ID of screw 80 mm) with an average solid residence time between 10 and 20 min. The whole system was purged with nitrogen to create an inert atmosphere before feeding the material into the reactors. The FMW was first pyrolyzed into an auger reactor, while the screws moved the material into the second stage post reformer.

The reaction started with no biochar. The biochar is formed during the reaction through the auger reactor section and is conveyed into the post reformer. Intermediate pyrolysis gases (organic vapors) are catalytically cracked within the reformer and enter the cooling system. The char effectively acts as a sacrificial catalyst. The weight hourly space velocity (WHSV) of FMW was estimated to be 1.3 1/h that is defined as the weight of feed per hour/weight of char (catalyst).<sup>24</sup>

The condensable organic vapors were condensed in two steps; first through a shell and tube heat exchanger circulating water as a cooling medium (cooling medium water glycol mixture cooled to −5 °C), second by means of an ice bath cooler. The incondensable gas entered the gas filtration system comprising of two wash bottles; one containing the aqueous phase and the second filled with cotton wool for aerosol capture. The cleaned permanent gas was detected by a gas analyzer and flared.

**2.3. Analytical Methods and Measurements.** Proximate analysis and ash content of the feedstock was calculated. Thermogravimetric analysis (TGA) using NETZSCH TG 209 F1 was done to determine the fixed carbon and volatiles according to ASTM E1131-03, while the ash and moisture content were calculated in line with ASTM E1755-01 and ASTM E1756-08 respectively, using a CARBOLITE muffled furnace. Inductively coupled plasma (ICP) metal analysis of ash was done by Medac Ltd.

Ultimate analysis (CHNSO\*) of the raw material, biocrude oil and biochar along with calorific values were performed by an external company Medac Ltd. The oxygen was calculated by difference (100% − ∑(CHNS + ash)).

The fuel properties, water content, TAN (total acid number), and viscosity of the TCR crude oil were determined by Monition Oil. The water content, TAN, and viscosity were measured in line with ASTM

D1744, ASTM D664, and ASTM D445, respectively. The gas composition was analyzed using an online gas detection system (MGA 12 from Dr. Födisch Umweltmesstechnik AG, Germany). The system was calibrated prior to the experiments, which consists of an infrared photometer (CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>x</sub>H<sub>y</sub>), an electrochemical cell (O<sub>2</sub>), and thermal conductivity detector (H<sub>2</sub>). The calorific value and density of the gas were measured with an online gas calorimeter—Union Instruments CWD 2005.

**2.4. GC-MS Analysis.** GC-MS analysis was carried out using an Agilent A7890 gas chromatograph followed by a Waters Micromass Ltd. GCT Premier Mass Spectrometer. A ZB5 Phenomenex column (30 m × 0.25 mm × 0.25 μm) was used for the analysis of the bio-oil. The gas chromatograph used for separation had a split ratio (1:10) using helium as a carrier gas with the flow rate of 1 mL/min. The initial temperature of oven was 50 °C and ramped up to 300 °C with a heating rate of 2.5 °C/min. A bio-oil sample was diluted in dichloromethane solution. The bio-oil compounds were identified by library searches (NIST libraries) and mass spectra evaluation.

## 3. RESULTS AND DISCUSSION

**3.1. Feedstock Characterization.** The proximate and ultimate analysis (determined on a moisture-free basis) of the FMW used in the TCR experiments are shown in Table 1. The

**Table 1. Feedstock Characterization**

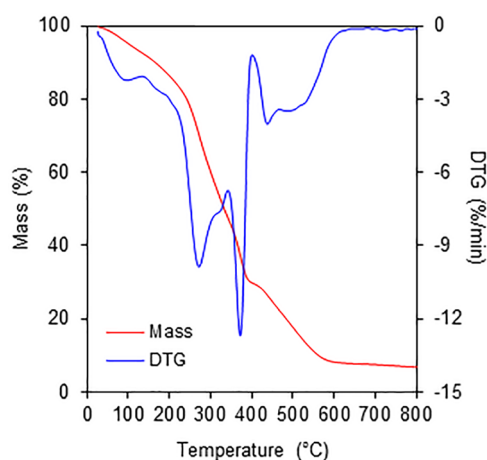
	unit	value
Ultimate Analysis (Moisture Free Basis)		
C	wt %	50.24
H	wt %	7.96
N	wt %	2.92
S	wt %	<0.10
O (difference)	wt %	34.18
Proximate Analysis (Dry Basis)		
moisture	wt %	13.09
ash	wt %	4.61
fixed carbon	wt %	5.12
volatiles	wt %	77.18
HHV	MJ/kg	23.25
LHV	MJ/kg	23.08

carbon, oxygen, and hydrogen contents are comparable to sewage sludge ultimate composition presented by Vassilev et al.<sup>25</sup> Due to high carbon and hydrogen contents, the dried food and market waste resulted in a gross calorific value of 23.25 MJ/kg which is comparable to sub-bituminous coal (24.4 MJ/kg). The fraction of volatile matter (VM) was also high up to 77% which is almost identical to the average composition of mixed waste paper 76.8%.<sup>25</sup>

Thermogravimetric (TG) analyses show mainly four stages of material loss (Figure 2). The initial weight loss began with the dehydration step where moisture was eliminated from the FMW between 30 and 105 °C (stage one). The second and third stages correspond to the decomposition of hemicellulose and cellulose, respectively.<sup>26</sup> They represent together the major mass loss indicated by the devolatilization of organic matter between 150 and 400 °C. The last peak on the DTG (stage four) is the devolatilization of polymers that occurs at temperatures over 400 °C.<sup>27</sup> The mass left behind is the char consisting of fixed carbon and ash. The mass of ash was determined from TGA combustion with an air atmosphere. The final ash content was 4.61 wt %.

**3.2. Mass and Energy Balance.** The mass balance has been calculated through standard eqs 1 and 2 and is shown in Figure 3a.





**Figure 2.** Weight loss behavior of the FMW with TG and DTG curves.

$$\sum \text{mass in} = \sum \text{mass out} \quad (1)$$

$$\sum \text{FMW} = \sum (\text{gas} + \text{char} + \text{condensate}(\text{bio-oil} + \text{aqueous phase}) + \text{losses}) \quad (2)$$

After the reaction, the products were completely accounted for, the residual mass loss is assumed to be negligible. Following the previous trends for product distribution reported in the TCR processing of wastes (MSW, digestate),<sup>21,28</sup> the FMW process produced permanent gases as the largest fraction (53 wt %). This is essentially due to thermal cracking of pyrolysis vapors at an elevated temperature in the post reformer which results in higher permanent gas yields.<sup>21</sup> The condensate liquid yield was 25 wt % of which 7 wt % oil was obtained after gravity separation and 18 wt % was aqueous phase liquid. The remaining char equated to 22 wt % and was the second largest product fraction in the process. This product distribution order is also in line with the catalytic pyrolysis of food waste by microwave heating which produced

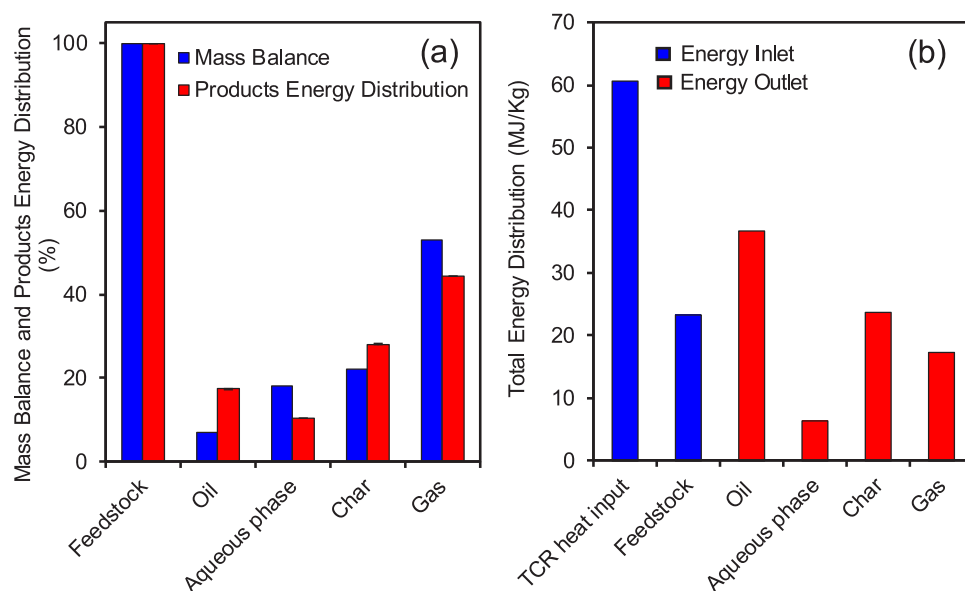
gas and char as the two greater fractions respectively. However, the reported mass balance is not comparable due to completely different processing mode and equipment.<sup>12</sup> Figure 3a also presents the energy distribution of the products calculated by the higher heating value (HHV) of the products and the mass balance of the process. The energy distribution showed that the energy was mainly transferred to the gases. Over 44% of the feedstock energy was recovered in the gas phase. The HHV of char showed a transition of 28% of the feedstock energy in the solid residue. Here, 18% and 10% of the energy from the feedstock were converted to the bio-oil and aqueous phase, respectively. The energy of the aqueous phase is the lowest recovered energy due to the low carbon content of the water phase. As a result, more than 70% of the feedstock energy is recovered in the gas and char phases.

The total energy balance of the entire system is shown in Figure 3b. The input energy includes the following: energy of TCR-2 ( $Q_{\text{TCR}}$ ) and feedstock energy ( $Q_{\text{F}}$ ). The output energy includes the following: chemical energy of the bio-oil ( $Q_{\text{B}}$ ), aqueous phase ( $Q_{\text{A}}$ ), char ( $Q_{\text{C}}$ ), and gas ( $Q_{\text{G}}$ ) and sensible heat loss ( $Q_{\text{H}}$ ). The heat loss is assumed to be negligible. At steady state conditions, the energy balance of entire system is as follows:

$$\sum (Q_{\text{TCR}} + Q_{\text{F}}) = \sum (Q_{\text{B}} + Q_{\text{A}} + Q_{\text{C}} + Q_{\text{G}}) \quad (3)$$

The conditions of the import and export were considered to be at standard values (25 °C and 1 atm), and all energy values (input and output) were calculated per kilogram of feedstock.<sup>29</sup> The chemical energies of feedstock, bio-oil, aqueous phase, char, and gas were calculated based on their HHVs. The TCR heat input for pyrolyzing of FMW was 60 MJ/kg which is 4.2 K·Wh/kg.

**3.3. Product Compositions.** Table 2 shows the TCR gas composition detected by the gas analyzer. The process generated gases with a higher heating value of approximately 17 MJ/Nm<sup>3</sup>. The high heating value was attributed to the high methane yields, and methane was found to be the greatest constituent within the gases reaching over 23 vol %. Methane



**Figure 3.** (a) Mass balance (weight percentage basis) and product energy distribution (energy percentage basis) and (b) total energy distribution of entire system.

Table 2. Permanent Gas Compositions

component	unit	average yield
H <sub>2</sub>	vol %	19.05
CO	vol %	17.54
CO <sub>2</sub>	vol %	18.27
CH <sub>4</sub>	vol %	23.49
C <sub>x</sub> H <sub>y</sub>	vol %	2.90
others	vol %	18.75
HHV	MJ/N·m <sup>3</sup>	16.88

yields increased at the expense of H<sub>2</sub>, which can be explained by a partial methanation of syngas over FMW biochar, or the hydrogenation of coke deposited on the biochar in the postreforming stage.

The selectivity of methanation reactions ( $C + 2H_2 \leftrightarrow CH_4$ ) could be triggered by the catalytically active biochar in the post reforming section of the TCR. Zu et al.<sup>30</sup> carried out methanation of syngas over a biochar supported catalyst. They effectively utilized rick husk derived activated biochar (ABC) as a catalyst support to Ru. The Ru/biochar catalyst showed excellent catalytic activity through the methanation of syngas. The selectivity of the methanation reaction reached 98% under the optimized conditions.<sup>30</sup> Similar results have also been reported by Wang et al.<sup>31</sup> during H<sub>2</sub> supplemented methanation of syngas over Ru/ABC catalyst. CH<sub>4</sub> yield and selectivity have been reported at 54% and 92%, respectively.<sup>31</sup> Taking the above studies into account, it can be hypothesized that the syngas would have partially catalyzed in the presence of catalytically active FMW biochar containing alkali and alkaline earth metals (AAEMs) to favor methane formation.

Similarly methanation reactions can also occur through coke deposited on the FMW biochar. Tar cracking over the pyrolysis biochar is very well documented in several studies which can also produce coke due to poly alkylation and condensation of aromatics in the gas phase.<sup>32</sup> As a result, the coke can deposit over the char and react with hydrogen to produce methane. The possibility of increased methane due to hydrogenation of coke can be supported by the findings of Maneewan et al.<sup>33</sup> who investigated the catalytic activity of pyrolyzed biochar on the product distribution and tar cracking in pyrolysis and hydro-gasification of wood. In both cases, they found a notable catalytic activity of biochar prepared at 750 °C which influenced the carbon conversion levels to higher syngas and methane yield (~ 6%) and lower CO formation (8.8%). They concluded that coke formed as a result of tar deposition on the biochar was hydrogenated to yield additional methane.<sup>33</sup> This effect can further be corroborated by Harvey et al.<sup>34,35</sup> who report tar cracking and the subsequent coking on the food-waste biochar.

Table 3 presents the FMW biochar composition (moisture free basis) and the metals retained within the char ash after thermo-chemical conversion of the FMW. The FMW biochar has proved more carbonaceous than the TCR biochars derived from MSW<sup>28</sup> and sewage sludge.<sup>36</sup> It had a higher heating value of 24 MJ/kg which is comparable to sub-bituminous coal.<sup>25</sup> ICP metal analysis showed that Ca was the major constituent in the biochar ash.

Table 4 presents the ultimate analysis (moisture free basis) and the fuel properties of the FMW bio-oil. The higher heating value (HHV) was estimated approximately 37 MJ/kg which is greater than woody biomass.<sup>22</sup> The highlighting point is the deoxygenation of the bio-oil (O <5 wt %) due to tar cracking

Table 3. FMW Biochar Composition and ICP Metal Analysis

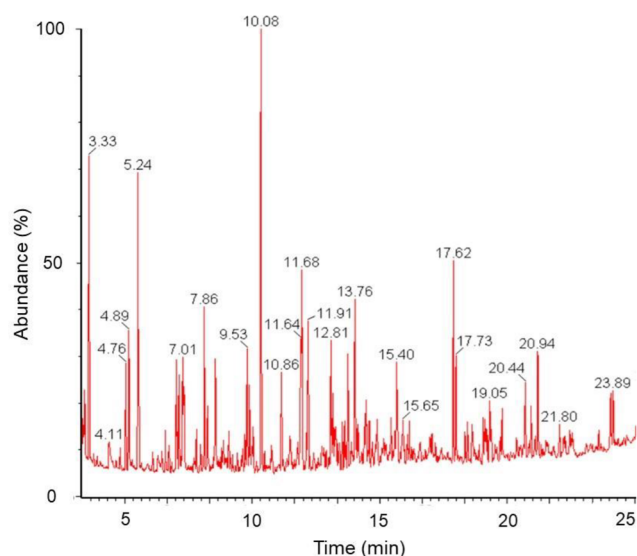
	unit	value
C	wt %	63.75
H	wt %	2.05
N	wt %	4.36
S	wt %	0.45
O (difference)	wt %	4.79
ash	wt %	24.6
HHV	MJ/kg	23.64
LHV	MJ/kg	23.47
Ca	%	9.64
Na	%	4.22
K	%	3.84
P	%	2.31
Fe	%	1.59
Mg	%	0.34
Al	%	0.26

Table 4. FMW Bio-oil Composition and Fuel Properties

	unit	value
C	wt %	81.48
H	wt %	7.41
N	wt %	6.34
S	wt %	0.68
O (difference)	wt %	3.85
ash	wt %	0.24
moisture	wt %	1.89
kinematic viscosity	cSt 40 °C	6.3
TAN (total acid number)	mg KOH/g	11.7
HHV	MJ/kg	36.72
LHV	MJ/kg	36.56

over the FMW biochar in the post reformer. Harvey et al. reported catalytic activity of food waste biochar to promote tar cracking. They used a mixture of activated food waste (FW) and coagulation-flocculation sludge (CF) biochars produced at 700 °C for the cracking of ethyl-benzene. The FW/CF biochar proved to be extremely effective with 85% tar conversion.<sup>34</sup> This biochar catalytic activity is ascribed to ash which is retained by the char. The ash contains inorganic species (K, P, Ca, Fe, Mg) which add a catalytic effect to the biochar.<sup>32</sup> As it can be seen in the Table 3 that the FMW char obtained at 700 °C postreforming temperature contains alkali metals which are known for tar tracking and deoxygenation at elevated temperatures. Ca and K are of the major metal constituents which were present in the FMW biochar; Ca is known for deoxygenating the bio-oil<sup>37</sup> while K suppresses the formation of long chain molecules.<sup>32,34</sup> Therefore, it can be inferred that Ca and K played their catalytic part in influencing the bio-oil composition and properties.

Figure 4 represents the GC-MS of FMW bio-oil, and Table 5 shows the major detectable chemical compounds in the FMW derived bio-oil. The bio-oil was largely composed of aromatic hydrocarbons such as toluene, benzene, naphthalene and its isomers, indene, fluorene, pyrene, etc. The higher aromaticity of the bio-oil may be explained by the high amount of protein in the FMW, where amino acids largely converted to aromatics due to scission in the polymer chain and cleavage of the side chain (R-group).<sup>38</sup>



**Figure 4.** GC-MS chromatogram of the FMW bio-oil and main compound detected.

**Table 5.** GC-MS (Polar Column) of the FMW Bio-oil (Organic Phase)

no.	compound	retention time (min)	relative abundance (%)
1	toluene	3.33	8.30
2	<i>p</i> -xylene	4.76	4.09
3	ethyl-benzene	4.79	2.65
4	styrene	5.24	11.39
5	benzene, 1-ethyl 2-methyl	7.01	4.45
6	indene	7.86	5.66
7	benzene,1-methyl-4-[1-propynyl]-	9.53	3.44
8	naphthalene	10.08	12.95
9	quinoline	10.86	3.35
10	naphthalene, 2 methyl	11.68	5.13
11	naphthalene, 1 methyl	11.91	5.70
12	biphenyl	12.81	3.77
13	acenaphthylene	13.76	6.27
14	fluorene	15.40	4.32
15	propane, 2-methyl-1,1-triphenyl	17.62	6.69
16	phenanthrene	17.73	3.68
17	pyrene	20.94	4.32
18	4-[1 <i>H</i> -indol-4[1,2-methyl]	23.89	2.01
19	demecolcine	26.86	1.82

Naphthalene was detected to be the most abundant aromatic compound within the oil, with a relative abundance of 12.95%. It appears that the oxygenated organic compounds were catalytically reformed into aromatics by the FMW char. Due to tar cracking and deoxygenation, the bio-oil was found to have less viscosity (6.3 cSt) and lower moisture (1.89 wt %).

The low water content (1.89 wt %) is an advantage as it will not cause further phase separation and instability problems during storage. However, the acid number was high due to the abundance of aromatics in the bio-oil. High acidity can cause corrosion in the components of the fuel system,<sup>39</sup> whereas the presence of high nitrogen in the bio-oil will promote NO<sub>x</sub> emission during combustion; therefore, it must be stripped out of the bio-oil prior to engine application.<sup>40</sup>

Table 6 shows the ultimate analysis of the FMW aqueous fraction of bio-oil (moisture free basis). The HHV of the

**Table 6.** FMW Aqueous Phase Composition

	unit	value
C	wt %	5.48
H	wt %	10.53
N	wt %	6.10
S	wt %	0.29
O (difference)	wt %	77.6
HHV	MJ/kg	6.22
LHV	MJ/kg	6.06

aqueous phase was estimated approximately 6 MJ/kg which is too low in comparison with the HHV of bio-oil (37 MJ/kg). The aqueous fraction contains high oxygen content in comparison with a bio-oil fraction which are 77 and 3.8 wt %, respectively. The aqueous phase of bio-oil is a complex mixture of oxygenated compounds including alcohols, acids, ketones, and aldehydes.<sup>41,42</sup>

Promising research has reported that the aqueous fraction of bio-oil can be used in wide range of applications such as crop growth promotion, crop pest control, deodorizing, composting, feed additives, coagulating, and antifungal agents.<sup>43,44</sup> As a result, water treatment is essential to remove all organic and acid compounds before disposal.

#### 4. CONCLUSIONS

The conversion of food and market waste (FMW) into biofuel via TCR can prove to be a sustainable pathway for the disposal of food and market waste. The conditioning of feedstock, drying in particular, is a prerequisite due to its high initial moisture content. The FMW biochar appeared to have cracked and reformed heavy molecular weight organic compounds which caused deoxygenation of the bio-oil. This reduces downstream processing requirements for oil upgrading if the oil is to be used as drop in fuels for transport. The bio-oil showed a high calorific value (37 MJ/kg) with a low viscosity (6.3 cSt) and low water contents (1.2 wt %). However, the FMW permanent gas composition was found to be lean in hydrogen and rich in methane which resulted in a high overall syngas calorific value. An energy dense char was also produced by the process which would be suitable to be used as a fuel in combustors and/or gasifiers. Overall, the experimental results are promising for waste conversion into sustainable fuels.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*Tel.: +44 (0) 121 414 5304. E-mail: [h.jahangiri@bham.ac.uk](mailto:h.jahangiri@bham.ac.uk).

##### ORCID

Miloud Ouadi: 0000-0003-1575-3163

Hessam Jahangiri: 0000-0001-5456-7019

Andreas Hornung: 0000-0002-9743-7561

##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

The authors would like to acknowledge the HORIZON 2020 flexJET Project for financial support. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No.

792216. We also thank the School of Chemistry at the University of Birmingham for their support for condensate liquid analysis.

## ■ ABBREVIATIONS

TCR = thermo-catalytic reforming  
FMW = food and market waste  
MSW = municipal solid waste  
AD = anaerobic digestion  
GHG = greenhouse gas  
CHP = combined heat and power  
PFD = process path flow diagram  
HHV = higher heating value  
LHV = lower heating value  
ABC = activated biochar

## ■ REFERENCES

- (1) Wilson, K.; Lee, A. F. *Philos. Trans. R. Soc., A* **2016**, 374 (2061), 20150081.
- (2) Jahangiri, H.; Osatiashiani, A.; Bennett, J. A.; Isaacs, M. A.; Gu, S.; Lee, A. F.; Wilson, K. Zirconia catalysed acetic acid ketonisation for pre-treatment of biomass fast pyrolysis vapours. *Catal. Sci. Technol.* **2018**, 8 (4), 1134–1141.
- (3) Shaheen, S. A.; Lipman, T. E. REDUCING GREENHOUSE EMISSIONS AND FUEL CONSUMPTION: Sustainable Approaches for Surface Transportation. *IATSS Research* **2007**, 31 (1), 6–20.
- (4) Li, S.; Yang, X. 20–Biofuel production from food wastes. In *Handbook of Biofuels Production*, second ed.; Luque, R., Lin, C. S. K., Wilson, K., Clark, J., Eds.; Woodhead Publishing: 2016; pp 617–653.
- (5) Du, C.; Abdullah, J. J.; Greetham, D.; Fu, D.; Yu, M.; Ren, L.; Li, S.; Lu, D. Valorization of food waste into biofertiliser and its field application. *J. Cleaner Prod.* **2018**, 187, 273–284.
- (6) Xu, F.; Li, Y.; Ge, X.; Yang, L.; Li, Y. Anaerobic digestion of food waste – Challenges and opportunities. *Bioresour. Technol.* **2018**, 247, 1047–1058.
- (7) Cerda, A.; Artola, A.; Font, X.; Barrena, R.; Gea, T.; Sánchez, A. Composting of food wastes: Status and challenges. *Bioresour. Technol.* **2018**, 248, 57–67.
- (8) Pham, T. P. T.; Kaushik, R.; Parshetti, G. K.; Mahmood, R.; Balasubramanian, R. Food waste-to-energy conversion technologies: Current status and future directions. *Waste Manage.* **2015**, 38, 399–408.
- (9) Skaggs, R. L.; Coleman, A. M.; Seiple, T. E.; Milbrandt, A. R. Waste-to-Energy biofuel production potential for selected feedstocks in the conterminous United States. *Renewable Sustainable Energy Rev.* **2018**, 82, 2640–2651.
- (10) Barik, S.; Paul, K. K. Potential reuse of kitchen food waste. *J. Environ. Chem. Eng.* **2017**, 5 (1), 196–204.
- (11) Parish, N. Food waste in England. In *The Environment*; House of Commons: England, 2017.
- (12) Liu, H.; Ma, X.; Li, L.; Hu, Z.; Guo, P.; Jiang, Y. The catalytic pyrolysis of food waste by microwave heating. *Bioresour. Technol.* **2014**, 166, 45–50.
- (13) Dahlin, J.; Herbes, C.; Nelles, M. Biogas digestate marketing: Qualitative insights into the supply side. *Resources, Conservation and Recycling* **2015**, 104, 152–161.
- (14) Santos, J.; Ouadi, M.; Jahangiri, H.; Hornung, A. Integrated intermediate catalytic pyrolysis of wheat husk. *Food Bioprod. Process.* **2019**, 114, 23–30.
- (15) Torri, I. D. V.; Paasikallio, V.; Faccini, C. S.; Huff, R.; Caramão, E. B.; Sacon, V.; Oasmaa, A.; Zini, C. A. Bio-oil production of softwood and hardwood forest industry residues through fast and intermediate pyrolysis and its chromatographic characterization. *Bioresour. Technol.* **2016**, 200, 680–690.
- (16) Bridgwater, A. V. *Environ. Prog. Sustainable Energy* **2012**, 31 (2), 261–268.
- (17) Papadakis, K.; Gu, S.; Fivga, A.; Bridgwater, A. V. Numerical Comparison of the Drag Models of Granular Flows Applied to the Fast Pyrolysis of Biomass. *Energy Fuels* **2010**, 24 (3), 2133–2145.
- (18) Elliott, D. C.; Biller, P.; Ross, A. B.; Schmidt, A. J.; Jones, S. B. Hydrothermal liquefaction of biomass: Developments from batch to continuous process. *Bioresour. Technol.* **2015**, 178, 147–156.
- (19) Yung, M. M.; Jablonski, W. S.; Magrini-Bair, K. A. Review of Catalytic Conditioning of Biomass-Derived Syngas. *Energy Fuels* **2009**, 23 (4), 1874–1887.
- (20) Jahangiri, H.; Bennett, J.; Mahjoubi, P.; Wilson, K.; Gu, S. A review of advanced catalyst development for Fischer–Tropsch synthesis of hydrocarbons from biomass derived syn-gas. *Catal. Sci. Technol.* **2014**, 4 (8), 2210–2229.
- (21) Neumann, J.; Binder, S.; Apfelbacher, A.; Gasson, J. R.; Ramírez García, P.; Hornung, A. Production and characterization of a new quality pyrolysis oil, char and syngas from digestate – Introducing the thermo-catalytic reforming process. *J. Anal. Appl. Pyrolysis* **2015**, 113, 137–142.
- (22) Jäger, N.; Conti, R.; Neumann, J.; Apfelbacher, A.; Daschner, R.; Binder, S.; Hornung, A. Thermo-Catalytic Reforming of Woody Biomass. *Energy Fuels* **2016**, 30 (10), 7923–7929.
- (23) Hornung, A.; Binder, S.; Jakuttis, M.; Apfelbacher, A. Anlage und Verfahren zur thermokatalytischen Behandlung von Material und damit hergestelltes. *Pyrolyseol* **2014**, 24.
- (24) He, M.; Xiao, B.; Liu, S.; Hu, Z.; Guo, X.; Luo, S.; Yang, F. Syngas production from pyrolysis of municipal solid waste (MSW) with dolomite as downstream catalysts. *J. Anal. Appl. Pyrolysis* **2010**, 87 (2), 181–187.
- (25) Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G. An overview of the chemical composition of biomass. *Fuel* **2010**, 89 (5), 913–933.
- (26) Buah, W. K.; Cunliffe, A. M.; Williams, P. T. Characterization of Products from the Pyrolysis of Municipal Solid Waste. *Process Saf. Environ. Prot.* **2007**, 85 (5), 450–457.
- (27) Gunasee, S. D.; Carrier, M.; Gorgens, J. F.; Mohee, R. Pyrolysis and combustion of municipal solid wastes: Evaluation of synergistic effects using TGA-MS. *J. Anal. Appl. Pyrolysis* **2016**, 121, 50–61.
- (28) Ouadi, M.; Jaeger, N.; Greenhalf, C.; Santos, J.; Conti, R.; Hornung, A. Thermo-Catalytic Reforming of municipal solid waste. *Waste Manage.* **2017**, 68, 198–206.
- (29) Zhao, X.; Zhang, J.; Song, Z.; Liu, H.; Li, L.; Ma, C. Microwave pyrolysis of straw bale and energy balance analysis. *J. Anal. Appl. Pyrolysis* **2011**, 92 (1), 43–49.
- (30) Zhu, L.; Yin, S.; Yin, Q.; Wang, H.; Wang, S. *Energy Sci. Eng.* **2015**, 3 (2), 126–134.
- (31) Wang, S.; Wang, H.; Yin, Q.; Zhu, L.; Yin, S. Methanation of bio-syngas over a biochar supported catalyst. *New J. Chem.* **2014**, 38 (9), 4471–4477.
- (32) Wang, N.; Chen, D.; Arena, U.; He, P. Hot char-catalytic reforming of volatiles from MSW pyrolysis. *Appl. Energy* **2017**, 191, 111–124.
- (33) Maneewan, K.; Kerkkaiwan, S.; Sunphorka, S.; Vitidsant, T.; Kuchonthara, P. Catalytic Effect of Biomass Pyrolyzed Char on the Atmospheric Pressure Hydrogasification of Giant Leucaena (*Leucaena leucocephala*) Wood. *Ind. Eng. Chem. Res.* **2014**, 53 (30), 11913–11919.
- (34) Hervy, M.; Villot, A.; Gérente, C.; Pham Minh, D.; Weiss-Hortala, E.; Nzihou, A.; Le Coq, L. Catalytic cracking of ethylbenzene as tar surrogate using pyrolysis chars from wastes. *Biomass Bioenergy* **2018**, 117, 86–95.
- (35) Hervy, M.; Weiss-Hortala, E.; Pham Minh, D.; Dib, H.; Villot, A.; Gérente, C.; Berhanu, S.; Chesnaud, A.; Thorel, A.; Le Coq, L.; Nzihou, A. Reactivity and deactivation mechanisms of pyrolysis chars from bio-waste during catalytic cracking of tar. *Appl. Energy* **2019**, 237, 487–499.
- (36) Conti, R.; Jäger, N.; Neumann, J.; Apfelbacher, A.; Daschner, R.; Hornung, A. *Thermocatalytic Reforming of Biomass Waste Streams* **2017**, 5 (1), 104–110.



- (37) Lin, Y.; Zhang, C.; Zhang, M.; Zhang, J. Deoxygenation of Bio-oil during Pyrolysis of Biomass in the Presence of CaO in a Fluidized-Bed Reactor. *Energy Fuels* **2010**, *24* (10), 5686–5695.
- (38) Kebelmann, K.; Hornung, A.; Karsten, U.; Griffiths, G. Thermo-chemical behaviour and chemical product formation from Polar seaweeds during intermediate pyrolysis. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 131–138.
- (39) Yang, Y.; Brammer, J. G.; Ouadi, M.; Samanya, J.; Hornung, A.; Xu, H. M.; Li, Y. Characterisation of waste derived intermediate pyrolysis oils for use as diesel engine fuels. *Fuel* **2013**, *103*, 247–257.
- (40) Arazo, R. O.; Genuino, D. A. D.; de Luna, M. D. G.; Capareda, S. C. Bio-oil production from dry sewage sludge by fast pyrolysis in an electrically-heated fluidized bed reactor. *Sustainable Environment Research* **2017**, *27* (1), 7–14.
- (41) Kechagiopoulos, P. N.; Voutetakis, S. S.; Lemonidou, A. A.; Vasalos, I. A. Hydrogen Production via Steam Reforming of the Aqueous Phase of Bio-Oil in a Fixed Bed Reactor. *Energy Fuels* **2006**, *20* (5), 2155–2163.
- (42) Black, B. A.; Michener, W. E.; Ramirez, K. J.; Biddy, M. J.; Knott, B. C.; Jarvis, M. W.; Olstad, J.; Mante, O. D.; Dayton, D. C.; Beckham, G. T. Aqueous Stream Characterization from Biomass Fast Pyrolysis and Catalytic Fast Pyrolysis. *ACS Sustainable Chem. Eng.* **2016**, *4* (12), 6815–6827.
- (43) Rui, Z.; Wei, D.; Zhibin, Y.; Chao, Z.; Xiaojuan, A. J. J. C. P. R. Effects of wood vinegar on the soil microbial characteristics. *Chem. Pharmaceut. Res.* **2014**, *6* (3), 1254–1260.
- (44) Baimark, Y.; Niamsa, N. Study on wood vinegars for use as coagulating and antifungal agents on the production of natural rubber sheets. *Biomass Bioenergy* **2009**, *33* (6), 994–998.