Biochar from Waste Derived Fuels as Low-Cost Adsorbent for Waste Hydrocarbons

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Abstract – The aim of this study is to prove technical feasibility of combined refuse derived fuel (RDF) torrefaction and oily wastewater treatment approach by using RDF derived biochar as a sorption media. Biochars prepared from refuse derived fuels in torrefaction, carbonization and pyrolysis modes were analysed as fuels and as hydrocarbon sorbents. Changes of elemental composition and properties of material during thermal treatment and subsequent washing process have been analysed. Experimental evaluation of sorption behaviour of toluene and diesel fuel on obtained biochar performed. Our results show that torrefaction/carbonization of RDF coupled with the subsequent washing of biochar is a method allowing to overcome absolute majority of the quality problems of waste derived fuels, including the most important one: high chlorine content. In spite the fact that optimal temperatures for upgrading waste derived fuels and to produce high quality sorbent does not coincide, technically it is possible to combine the washing of torrefied/carbonized waste derived fuels with the treatment of wastewaters that are polluted with oils or hydrocarbons.

Keywords – Absorption; carbonization; emulsified wastes; RDF (Refuse derived fuel); torrefaction

Nomenclature

m	Mass	kg
HHV	Higher heating value	MJ/kg
Δm_{tot}	Total extracted amount	g
C	Concentration of substance	mg/g
V	Volume	ml
Q	Sorption capacity	g/g
W	Mass of sorbent	g
q	Absorbed amount of substance	g
t	Time	min
k_1	Reaction rate constant	1/min

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1. INTRODUCTION

Generation of solid organic wastes is one of the greatest challenges of today. By 2025 worldwide production of municipal solid wastes can reach approximately 2.2 billion tons per year, of which in average 46 % are formed by biomass, 17 % by paper and 10 % by plastics [1]. Production of waste derived fuels from the organic fraction of unrecyclable post-consumer waste is widely accepted and have showed the ability to help us to “close the loop” in the whole waste recovery mind-set [2]. While in the same time, waste derived fuels usually are of very low quality due to high moisture content, low energetic value, high heterogeneity, presence of unwanted elements and complex structure, preventing effective grinding of this material [3], [4]. In this respect as prospective can be considered carbonization and torrefaction of the organic part of municipal solid waste. Recent studies have showed that pyrolytic pre-treatment such as torrefaction or carbonization is able to upgrade properties of waste derived fuels significantly [5]–[8]. Usually torrefaction is defined as a slow heating of biomass or waste derived feedstock in an inert environment and temperature range of 200–300 °C [9]–[11]. The fundamental principle of torrefaction is preferential and selective degradation of lower calorific fraction present in the feedstock [12]. Furthermore, as it is pointed in [13], 90 % of chlorine contained in PVC may be removed by torrefaction at 260–300 °C due to transformation of mentioned substance from the organic form into hydrochloric acid and its subsequent evaporation.

The study [8] have showed, that thermal treatment of waste derived fuels itself is not able to deal with high chlorine content, while excessive chlorine may be removed using water leaching after the pyrolysis. It is clear, that the use of clean water in leaching process is unwanted from economic as well as from environmental point of view as it is resulting in high volumes of wastewaters.

Liquid wastes consisting of water and hydrocarbons and/or oils as well must be viewed as serious environmental problem of today, large amount of such wastes is generated on daily basis from various industries [14]. Such waste emulsions may cause technical problems in wastewater treatment plants as well as to have a negative influence on the quality of the wastewater treatment plant effluent. Therefore, oil content reducing measures must be taken before release of such by-product into municipal waste treatment units or the environment [15]. Conventional gravitational techniques like gravity settling, centrifuges, and air flotation, are not effective enough for the separation of oil-in-water emulsions [14]. Recently multiple modern methods of de-emulsification such as the use of magnetic particles as the demulsifying agent [16], filtration membranes made from polymers with specific wetting properties (simultaneous hydrophobicity/oleophilicity) [17], [18] while in spite to the technical complexity of these methods all of them expresses similar drawback: they fit into linear ‘take–make–dispose’ approach. Today linearity must be viewed as obsolete concept: the aim of XXI century is to close the loop and to redefine refuse as resource [19]. Adsorption and coalescence filtration are promising choice of treatment of oily wastewaters for its simplicity, effectiveness and feasibility when appropriate sorbent is used [20]. Bio-chars obtained as a result of thermochemical processes have showed good sorption properties, exceeding the quality of industrial products by certain indicators [21].

The aim of this study is to prove technical feasibility of combined RDF torrefaction and oily wastewater treatment approach by using RDF torrefaction/carbonization biochar as a sorption media.

2. MATERIALS AND METHODS

2.1. Torrefaction / Carbonization

Samples of RDF were collected in 5 waste processing facilities in Latvia and Estonia, the names of facilities are not disclosed; technical methods used in preparation of studied RDFs are showed in Table 1. Collection of samples performed after the shredder (or after bio treatment in some cases). In every factory, 20 samples (around 1 kg each) were taken and then mixed. The dominant fraction in all samples was the plastic fraction, fractional composition of samples is demonstrated in Fig. 1. Samples were shredded to particle size <1 mm to reduce an error caused by the inhomogeneity of material. Thermal treatment performed in closed steel cylinders filled with nitrogen, in laboratory oven, at 200, 300, 400 and 500 °C. The mass of the sample in the reactor was 50 g. The heating rate was 20 °C/min, the heating time (sum of heating up and holding times) was 3 hours in all cases. Natural cooling down was applied after the treatment.

Fig. 1. Composition of used RDFs.

2.2. Characterization of biochar

Calorific value was determined according to standard method [22] by using bomb calorimeter *Berthelot Mahler, I.S.Co* at constant volume.

Nitrogen, carbon and hydrogen content determined according to standard method [23] using a *Thermo Fisher Scientific Flash EA1112* Series analyser. Five measurements per sample are carried out. The tin capsule with sample is inserted into the combustion reactor, where the sample is combusted in the presence of oxygen and catalyst. After the combustion reaction, the gaseous products (CO_2 , H_2O , NO_x) are transferred by a helium flow through the copper. Copper reduces nitrogen oxides to nitrogen and removes excess oxygen (CuO). The gases then flow through a column where the gases are separated and detected. As a result, the hardware program outputs the percentage composition of the elements. The elemental composition is determined by comparing the sample with a standard substance (acetanilide $\text{C}_8\text{H}_9\text{NO}$) and a reference factor called K-factor. Oxygen content calculated considering results of described measurement and ash content.

Sulphur and chlorine content determined according to standard method [24], by digestion in calorimetric bomb (*Berthelot Mahler, I.S. Co*) and photometric detection by a *Pharo100 Spectroquant*.

Proximate analysis was made using thermogravimetric method described in [25], in 5 replicates, results averaged.

Mass yields calculated using the Eq. (1).

$$M_{yield} (\%) = \frac{m_{char}}{m_{RDF}} \cdot 100 \quad (1)$$

TABLE 1. TECHNOLOGICAL APPROACHES USED FOR THE PREPARATION OF ANALYSED RDFS

Sample	Description
RDF 1	Mixed municipal waste is screened, metals separated. Then leftovers are sorted by means of manual sorting and air stream, then fine shredded.
RDF 2	Mixed municipal waste is shredded (200–400 mm), metals separated. Then waste is screened on vibrating screen and in trommel drum. Light fraction is separated by air stream, then fine shredded.
RDF 3	Mixed municipal waste is shredded, metals separated, then leftovers screened using trommel drum. Coarse fraction is sorted manually and by means of air stream. Then fine shredded.
RDF 4	Mixed municipal waste is shredded and screened 60 mm. Then fine shredded. No biotreatment performed.
RDF 5	Mixed material waste is shredded and stored in naturally ventilated large heaps for few months. Then screened (40 mm) and fine shredded.

Energy yields calculated using the Eq. (2).

$$E_{yield} (\%) = M_{yield} \cdot \frac{HHV_{char}}{HHV_{RDF}} \cdot 100 \quad (2)$$

Sample surface was analysed by Brunauer-Emmett-Teller (BET) method [26], using a Quadrasorb SI gas sorption analysis system (Quantachrome Instrumentis, Boynton Beach, USA). Liquid nitrogen (at $-196\text{ }^{\circ}\text{C}$) was applied for the physical sorption-desorption isotherms.

2.3. Washing of Biochar

Samples of RDFs torrefied ($300\text{ }^{\circ}\text{C}$) as described before were used. Around 2.5 g of samples have been weighed in a cellulose capsule and sealed with glass fiber. Afterwards the capsules were placed in a Soxhlet extraction unit (*Behr Labor-Technik*), distilled water was used as a solvent, and the procedure was applied for 8h. After extraction the water was collected, its volume (V) measured. The capsules were dried and weighed, the total extracted amount (Δm_{tot}) was calculated. Concentrations (C) of 25 different elements (Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sr, V, Zn) were quantified in water phase by using ICP-OES (*Thermo Scientific iCAP 7000* series).

Sulphate ion (SO_4^{2-}) determined as follows: 25 mL of filtered sample was added to an Erlenmeyer flask, 2.5 mL of conditioning reagent was added, as well as a pinch of BaCl_2 . The solution was mixed and after 5 minutes was measured on a spectrophotometer (*Hach-Lange DR2800*) at 450 nm wavelength (*Hach®* method 680). Distilled water was used as a blank. Concentration (C) determined according to the calibration curve.

Bicarbonate (HCO_3^-) determined as follows: 50 mL of sample was transferred to a 250 mL flask and 5 drops of methyl orange indicator was added. The sample was titrated with 0.1 N HCl. Experiments were run in triplicate. Results were calculated after titration results.

Chloride ions (Cl^-) determined as follows: 50 mL of sample was transferred to a 250 mL flask and 1 mL of 10 % K_2CrO_4 solution was added. The sample was titrated with 0.02 N AgNO_3 . Experiments were run in triplicate. Results were calculated from titration results.

The amount of insoluble CaCO_3 formed in the water phase during the process estimated by using gravimetric method.

The percentage of every substance in total dissolved substance calculated by using the Eq. (3).

$$w(\%) = 100 - \left[\frac{\Delta m_{\text{tot}} - \frac{c}{1/V}}{\Delta m_{\text{tot}}} \cdot 100 \right] \quad (3)$$

2.4. Toluene Adsorption Study

Headspace Gas Chromatography (HS-GC). A *TurboMatrix 40 Trap* automatic HS injection system coupled with the *Clarus 580 GC* unit equipped with a flame ionization detector (FID) was used. The injection port of the GC system was operated at 220 °C, split less mode, and 35 psi of pressure. A flame ionization detector was employed with hydrogen and air flow rates of 45 and 450 mL/min, respectively. Helium at 20 cm/s linear velocity was the carrier gas. The detector temperature was set at 250 °C. The headspace operating conditions were as follows: 5 min shaking for the sample equilibration at a temperature of 75 °C; needle temperature of 180 °C; vial pressurization time of 0.5 min; vial pressure of 40 psi; sample loop filling time of 1.6 min, trap low and high temperature 50 °C, 290 °C; trap hold time 5.0 min; desorb time, 0.5; desorb pressure, 35 psi; transfer line temperature of 180 °C; dry purge time, 0.5 min; and GC cycle time 24.8 min.

GC separation was carried out on a SPB-624 Capillary Column (60 m × 0.25 mm × 1.4 µm; *Supelco*). Toluene was determined by the temperature program of the oven which was initially holding at 60 °C for 1 minute, increasing by 4.0 °C/min to 155 °C.

The produced powdered bio-char samples (250 mg) were thoroughly mixed with of 5.0 ml deionized water hermetically sealed in a 21.6 mL glass bottle with toluene to obtain solution at approximately 877–43831 mg/L concentration (toluene solubility 535 mg/L). The resulting solution was stirred 6 and 24 hours in the shaker by room temperature. The solution was then filtered on a membrane filter (0.45 µm) in no permeable vial (21.6 mL) and 3.0 ml by volume filtrate directly submitted to HS-GC analysis.

2.5. Diesel Adsorption Study

The sorption study was carried out in a batch system at room temperature. Using stainless steel net 0.1 g of sorbent was immersed into the glass beaker, filled with 50 mL of diesel fuel. After 30 min of sorption the wet sorbent was taken out, then drained for 2 min in air, and finally dried using filter paper and weighted. The diesel fuel sorption capacity for sorbent were obtained based on following Eq. (4) [27]–[29].

The effect of sorbent dosage on the amount of sorbed diesel fuel was studied by using sorbent mass between 0.05 g and 2 g.

$$Q = \frac{w_2 - w_1}{w_1}, \quad (4)$$

where

- Q Sorption capacity of diesel fuel, g/g;
 w_2 Mass of wet sorbent after sorption, g;
 w_1 Mass of the sorbent before sorption, g, each sample was measured 3 times.

Sorption kinetics study of diesel fuel on RDF sorbents. Using stainless steel net 0.1 g of sorbent was immersed into the glass beaker, filled with 50 mL of diesel fuel. The sample and net were taken out at different time intervals (10 s, 30 s, 1 min, 1.5 min, 2 min, 6 min, 15 min, 30 min, 1 h and 24 h). The wet material was drained and weighted as previously mentioned.

3. RESULTS AND DISCUSSION

3.1. Characterization of Biochar

Changes in feedstock composition during the low temperature torrefaction (200 °C) were insignificant, mass lose was only 4 % (Fig. 2), colour of material remained unchanged, no signs of carbonization observed. In spite to the small increase of calorific value (energy yield: 101.2 %) treatment in low temperature torrefaction regime seems to be senseless for the treatment of refuse derived fuel. In turn, high temperature torrefaction (300 °C) provided significant changes of material, 15 % mass lose and energy yield 93.5 % (Fig. 2.). Slight decrease in volatile matter, carbon and oxygen content as well as increase of fixed carbon and ash levels observed (Table 3). Removal of chlorine that have been observed by [5] during the torrefaction treatment of small RDF samples under conditions of purging nitrogen gas was not observed in our experiment. This fact coincides with the findings of [8] and demonstrates that fixed bed torrefaction is able only to transform organic chlorine into inorganic form but is not able to remove it due to absorption of the formed hydrochloric acid on surrounding material. Thermal treatment of RDF in carbonization (400 °C) regime seems to be excessively aggressive if the only objective is to increase the quality of the solid product. This finding is completely compliant with the results of [30]. This treatment regime results in strong transformation of the fuel and almost complete removal of the plastics: the fraction with the highest energetic value. Therefore, energy yield in this case is too low (Fig. 2) but resulting ash content value is too high (Table 3). Such treatment seems to be useful only if the process is organized in a way able to produce marketable product not only from the resulting solid fraction, but from volatiles as well. Treatment in pyrolysis regime (500 °C) seems to be the only one that is able to increase the surface area of obtained bio-char (Table 3), while in the same the time fuel value of the solid residue in this case is very low (Table 3, Fig. 2).

3.2. Washing of Biochar

Results of washing experiment of torrefied RDF have showed that the combination of torrefaction and subsequent washing is much more effective method for the improvement of RDF quality than torrefaction alone. Washing results in the removal of soluble Ca, Na and K salts (bicarbonates, sulphates and chlorides) from the material, in the same time amounts of other metals in the washed away fraction do not exceed 1 % (Fig. 3). Active formation of the insoluble calcium carbonate containing substance is observed during the washing process. As it is showed in Fig. 4, washing significantly increases the calorific value of torrefied waste derived fuels by reducing its ash content. Furthermore, this process almost completely

removes chlorine, being the worst quality problem of RDF, inducing severe operational issues, including boiler corrosion and production of problematic emissions such as hydrochloric acid and dioxins during the combustion [31]. Washing also significantly reduces sulphur content, also is responsible for corrosion issues in incineration plants [32].

TABLE 3. COMPOSITION AND PROPERTIES OF INITIAL RDF AND OBTAINED BIOCHARS

	N, %	C, %	H, %	O, %	Volatiles, %	Fixed carbon, %	Ash, %	BET surface area, m ² /g
RDF	1.1 ± 0.7	56.1 ± 3	4.4 ± 0.5	21.4 ± 7	76.0 ± 2	5.8 ± 2	15.8 ± 2	–
RDF 300 °C	1.2 ± 0.7	50.5 ± 3	4.3 ± 0.5	16.8 ± 7	63.3 ± 2	11.2 ± 2	26.4 ± 2	0.8
RDF 400 °C	1.1 ± 0.7	44.3 ± 3	4.0 ± 0.5	7.2 ± 7	38.2 ± 2	17.8 ± 2	42.2 ± 2	0.5
RDF 500 °C	1.5 ± 0.7	26.0 ± 3	3.5 ± 0.5	9.3 ± 7	19.8 ± 2	19.8 ± 2	58.4 ± 2	49.6

Fig. 2. Mass and energy yields in solid residue as a result of treatment at different temperatures.

Fig. 3 Composition of the part of biochar dissolved as a result of washing.

Fig. 4. Changes in composition and properties of RDFs during torrefaction and subsequent washing.

3.3. Characterization of Sorption Properties of Biochar

Toluene sorption were investigated on biochars produced at various temperatures. Fig. 5. displays the sorption data, experiments were performed at room temperature for 24 h. Obtained results show differences between sorbents that are heated at temperatures from 300 °C to 500 °C. Although the form of all isotherms is similar, they exhibit a very unfavourable trend, with an almost square convex shape to the concentration axis (C_e). The sorption isotherm representing sorbed amount of toluene onto biochar sorbent heated at 300 °C is convex to the axis of equilibrium concentration of toluene up to a concentration value about 410 mg/L, very similar to that also isotherm of biochar heated at 400 °C is convex to axis of equilibrium concentration up to concentration value about 370 mg/L. Different properties are observed for the sample heated at 500 °C temperature – it has considerably higher surface area in comparison to the samples heated at 300 °C and 400 °C temperature and the point of inflexion is shifted towards lower concentration value of toluene and is observed at the value of 320 mg/L. These isotherms show that toluene uptake increases exponentially with increasing concentration. According to [33] the shapes of obtained isotherms fall within type III, and according to [34] classification the isotherms follow S type curve pattern. The initial direction of curvature indicate that adsorption become easier with the rise of sorbate concentration. The more sorbate is absorbed, the easier it is for additional amounts of sorbate to bound to the sorbent; thus, S curves indicate to side-by-side association between absorbed species, thus ensuring adhesion to the surface of the sorbent. According to [34] curves indicate vertical orientation of adsorbed molecules at the surface, the solute molecule is monofunctional and meets strong competition for sorbent sites, from molecules of solvent or of another adsorbed species.

The sorbed amount of diesel fuel is increasing with increase of sorbent dose from 0.05 g to 0.5 g (Fig. 6). The maximum diesel fuel sorption capacity of biochar is 2 g/g. The initial increasing trend can be explained by the increase in surface area – number of available sorption sites increases by increasing the sorbent dose. Further increase in sorbent dose over 0.5 g reduced sorption capacity of biochar. The decrease in sorption capacity with increase in sorbent dose could be due to the high number of unsaturated sorption sites. As sorbent weight increases possible is material compacting which may decrease ability of diesel fuel to penetrate the material evenly, as well as sorbent surface aggregation may occur as a result surface area may decrease, diffusional holes may be blocked, and sorption sites may be unsaturated [35]. The results of our study agree with other studies using different materials for diesel fuel removal (Table 4). However, it is worth to mention that experimental conditions like sorbent dosage, initial concentration, pH, ionic strength, sorption time and temperature significantly affect sorption process and consequently also maximal sorption capacity. Sorption kinetics gives valuable insight in the pathway of sorption process and sorption mechanism. The sorption kinetics of diesel fuel on heated biochar samples was studied as a function of time at room temperature. Sorption capacity increases with increasing sorption time until it reaches the maximum of 2.55 g/g after 24 h. According to the results of sorption kinetics study (Fig. 7), the rate of diesel sorption is very high at the beginning – most of the diesel fuel are sorbed within first 6 min (sorbed amount reach 1.9 g/g). After that the rate of the diesel sorption is gradually reduced and become steady. During the first 10 min sorption capacity increased rapidly which may be due to availability of sorption sites on the surface of the sorbent, but as the surface of the sorbent becomes saturated with molecules of sorbates the sorption rate tends to decrease. Additional experiment was carried out at 24 h and sorbed amount of diesel fuel slightly increased, reaching 2.55 g/g.

TABLE 4. COMPARISON OF DIESEL SORPTION CAPACITIES

Sorbent	Sorbate	Sorbed amount, g/g	Reference
sawdust	diesel	1.6	[36]
straw	diesel	3,9	[36]
wool	diesel	5.6	[36]
moss	diesel	6.2	[36]
peat	diesel	6.3	[36]
sapropel	diesel	2.5	[37]
luffa	diesel	6–12	[38]
peat biochar	crude oil	5.9–8.6	[39]
peat	crude oil	3.5–6	[40]
oil palm leaves	crude oil	1.18	[41]
MSW biochar	toluene	0.000850	[42]
activated carbon	toluene	0.209	[19]
biochar	toluene	0.178	[19]

Fig. 5 Toluene sorption on biochar, sorption time 24 h.

Fig. 6. The effect of sorbent dosage, sorption time 30 min.

Fig. 7. Sorption kinetics of diesel fuel, sorbent dose 0.1 g.

Kinetic models are often used to characterize sorption process. In order to explore mechanisms of sorption and potential rate controlling steps, for example chemical reaction processes and mass transport pseudo-first-order, pseudo-second order models have been applied to evaluate the experimental data. Appropriate sorption model was determined comparing the determination coefficients in the pseudo-first and pseudo-second-order equations.

Pseudo first order reaction is expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (5)$$

where

q_e	Diesel fuel sorbed at equilibrium, g/g;
q_t	Diesel fuel sorbed at time t , g/g;
t	Time, min;
k_1	Reaction rate constant, 1/min.

Pseudo-first-order reaction rate constant can be determined from the slope of the $\ln(q_e - q_t)$ vs t graph.

Pseudo second order reaction is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}, \quad (6)$$

where k_2 – the reaction rate constant (g/g min); pseudo second order reaction rate constant (k_2) can be determined from the slope of the t/q_t vs t graph [43].

The linear regression coefficient of determination (R^2) and parameters of the pseudo-first and pseudo-second order reactions were calculated. Experimental data showed that the pseudo-second-order kinetic model could explain the sorption process of diesel fuel on biochar better than pseudo-first order model since the correlation coefficients R^2 were 0.997, 0.998 and 0.999 for samples heated at 300 °C, 400 °C and 500 °C accordingly. The experimental values q_e exp agreed well with the estimated q_{eq} – 1.32 g/g, 1.70 g/g and 2.48 g/g (at corresponding temperatures 300 °C, 400 °C and 500 °C heated samples) values calculated from the pseudo-second order equation, and finally estimated reaction rate constant k_2 – 0.21 g/g min for 300 °C heated sample, k_2 – 0.47 g/g min (400 °C) and k_2 – 4.76 g/g min (500 °C).

4. CONCLUSIONS

Torrefaction/carbonization coupled with the subsequent washing of biochar is a method allowing to overcome absolute majority of the quality problems of waste derived fuels, including the most important one: high chlorine content. Solid fuel obtained as a result of such approach is clean and technically and environmentally safe. Technically it is possible to combine the washing of torrefied/carbonized waste derived fuels with the treatment of wastewaters that are polluted with oils or hydrocarbons. In spite the fact that optimal temperatures for upgrading waste derived fuels and to produce high quality sorbent does not coincide, torrefaction/carbonization of RDF produce biochars that are prospective as low-cost sorbents. RDF derived biochar exhibits good sorption properties towards toluene. The maximum diesel fuel sorption capacity of biochar is 2 g/g. The results of sorption kinetics of diesel fuel on biochar indicate that sorption capacity increases with increasing sorption time until it reaches the maximum of 2.55 g/g after 24 h. The theoretical equilibrium sorption capacities obtained by fitting the pseudo second-order kinetic were very close to the experimental values.

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