



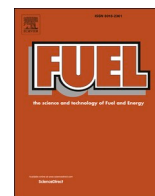
Thermochemical recycling of tall oil pitch in a dual fluidized bed

Downloaded from: <https://research.chalmers.se>, 2025-12-04 23:28 UTC

Citation for the original published paper (version of record):

Cañete Vela, I., González Arias, J., Berdugo Vilches, T. et al (2023). Thermochemical recycling of tall oil pitch in a dual fluidized bed. Fuel, 340. <http://dx.doi.org/10.1016/j.fuel.2023.127596>

N.B. When citing this work, cite the original published paper.



Thermochemical recycling of tall oil pitch in a dual fluidized bed

Isabel Cañete Vela^{*}, Judith González-Arias, Teresa Berdugo Vilches, Martin Seemann, Henrik Thunman

Department of Space, Earth and Environment (SEE), Division of Energy Technology, Chalmers University of Technology, 412 96 Gothenburg, Sweden

ARTICLE INFO

Keywords:

Tall oil pitch
Carbon recycling
Fluidized bed
Steam cracking
Thermochemical recycling

ABSTRACT

Crude tall oil is a by-product obtained from the manufacture of chemical wood pulp. The residue obtained after the distillation of this product is known as tall oil pitch (TOP). This complex fraction is a highly viscous liquid that consists mainly of free fatty acids, fatty acids derivatives, rosin acids and additives. Given its complex composition, it is commonly used as fuel for heat production. In this work, steam cracking is proposed as an alternative treatment for this residue. Steam cracking can convert TOP into a valuable product gas that can be used in different applications including the production of green chemicals, moving towards a carbon circular economy. The experimental tests were performed in the Chalmers pilot scale Dual Fluidized Bed, consisting of a steam cracker and a combustor. For these experiments, the thermochemical decomposition of 150–175 kg/h TOP was performed at the steam cracker at two different temperatures (775 and 825 °C) to evaluate the influence of this parameter on the obtained products. Wood pellets were also tested as reference material for the highest temperature. The distribution of the obtained products was analysed. Results show that TOP can be regarded as a by-product instead of a residue and used as feedstock for the recovery of chemical building blocks and syngas via thermochemical recycling. Between 40 and 50 % of the carbon present in the fuel is kept in the permanent gases, while about 20 % is in aromatic hydrocarbons. Compared to biomass, the aromatics yield obtained for TOP is much higher (190 g/kg for TOP and 13 g/kg for biomass). Among the species found, benzene, toluene and xylene, represent between 62 and 72 % of the total measured aromatics. Regarding the gas fraction, the production of valuable light hydrocarbons (such as ethylene and propylene) is more pronounced in the TOP residue than in the biomass. In addition, an energy balance over the system was estimated and showed that TOP thermochemical recycling can be self-sustained in a Dual Fluidized Bed if the non-valuable products are combusted. The results obtained in this work indicate that this TOP could be an appealing option to consider as a source of biorefinery revenue leading to the circular use of waste.

1. Introduction

A sustainable framework should consider not only the reduction of greenhouse gas (GHG) emissions, but also to decrease dependency on fossil fuels and to promote a circular economy. The substitution of fossil resources with biomass can reduce the use of fossil fuels, but its potential is limited due to trade-offs with sustainability [1]. Biomass scarcity is an argument for adopting circular economy principles for the management of biomass: to minimize virgin resource use, as well as to reduce the negative impacts caused by losses. A circular bio-economy emphasizes the use of renewable energy sources and sustainable management of ecosystems, setting limits on biomass usage in society [1,2].

An example of a circular bio-economy is the distillation of crude tall oil into chemicals. Crude tall oil (CTO) is a by-product obtained from

chemical wood pulp manufacturing. It is considered the most important side product of the kraft pulping process in softwood and mixed wood pulp mills, which after refining and fractionation, offers several base chemicals for the process industry as shown in Fig. 1. In Europe, it is estimated that about 650 k tons of CTO are available per year [4]. It is a commercially valuable by-product that contains rosins, unsaponifiable sterols, rosin acids and tall oil pitch (TOP) as main fractions [5]. As a bio-based material produced mostly from softwood trees (e.g., pine and spruce) the distribution of the fractions obtained from CTO vary accordingly to the geographical location and/or the type of trees. According to Cashman et al., the usual composition for the European fractions is tall oil fatty acids (34 %), tall oil rosins (27 %), distilled tall oil (11 %) and tall oil pitch (28 %) [6], where TOP can reach up to 37 % [4,6]. This last fraction has been typically used for energy recovery and

^{*} Corresponding author.

E-mail address: canete@chalmers.se (I. Cañete Vela).

<https://doi.org/10.1016/j.fuel.2023.127596>

Received 28 October 2022; Received in revised form 29 December 2022; Accepted 22 January 2023

Available online 28 January 2023

0016-2361/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

it is often returned to the pulp mill to be used as fuel, leading to greenhouse gas emissions. Alternatively, some upgrading methods have been developed making the TOP suitable to produce sterols or rubber softeners [7]. However, the utilization of this residue is still an unsolved problem due to the many processes that are involved in its upgrading and purification.

When it comes to its overall composition, about 70 % of the total TOP fraction is composed of free and esterified acids [8]. The chemical structure of these acids, mainly aliphatic, makes TOP a potential feedstock to produce chemical building blocks such as ethylene, propylene, benzene, etc. These building blocks coming from waste products are a desirable contribution for the chemical industry when circular economy approaches are considered [9]. An example of a potential synergy between waste upgrading and the production of chemicals can be found in the plastic manufacturing industry. Currently, the production of chemical building blocks at an industrial scale comes from fossil fuels. Nevertheless, the severe climate mitigation guidelines that comprise phasing out fossil-based carbon, will most likely entail the increased use of biogenic carbon. Nowadays, the main use of TOP is as fuel, which allows the recovery of energy, but does not involve the circular use of the carbon atoms that are present in this product. If the European Union's Waste Framework Directive is followed, the recovery of valuable chemicals is preferred over energy recovery. In this sense, thermochemical recycling arises as a suitable way to fulfil this objective, since it is possible to recover the chemical building blocks of the feedstock leaving them available for its further use in the chemical industry [10]. Nowadays, the most usual method to obtain these building blocks that are used in the chemical industry is through steam cracking of fossil-based hydrocarbons [11]. The similarities in terms of the chemical structure of fossil naphtha and the aliphatic chains present in the TOP makes this product an appealing alternative feedstock for thermochemical processes allowing the direct production of the required chemical building blocks.

However, due to the double bonds in the aliphatic hydrocarbon bonds and the aromatic structures that are also present in the TOP composition, it is expected that the yield of aromatic products is higher than that for saturated hydrocarbons [12]. This fact can lead to blockages and coke deposition in the usual industrial furnaces (i.e., existing

tubular cracking units). For this reason, a reactor configuration that can handle coke deposition is required for thermochemical treatment of this kind of waste. The dual fluidized bed (DFB) configuration is deep-rooted for the conversion of carbonaceous materials offering a wide range of opportunities regarding the selection of feedstock [13–15]. A DFB system consists of two interconnected fluidized bed reactors (a combustor and a steam cracker) allowing the circulation of the bed material between them. This favours the removal of the coke deposits, since the bed material is continuously oxidized on the combustion side [16], while also being resistant to feedstock impurities. In the cracker, the fuel decomposition into valuable products such as syngas and ethylene occurs in the presence of steam, while the non-valuable products can be combusted in the combustor generating the heat for the process.

In this work, the main aim was to evaluate the feasibility of recycling the TOP waste in a DFB system by recovering valuable chemical building blocks. To this end, the product distribution obtained after the thermochemical decomposition in the pilot-scale steam cracker of TOP was assessed. For comparison, the product distribution obtained from biomass is also presented in this study. Two different temperatures were selected to evaluate the effect of the temperature on the product yields and the carbon distribution. In addition, the energy balance over the DFB is studied to know if additional energy input is necessary to sustain the process or if the non-valuable products can be combusted to produce sufficient energy to sustain the process.

2. Materials & methods

2.1. Feedstock

Tall oil pitch (TOP) is a complex fraction obtained from the vacuum distillation of crude tall oil. The product consists mainly of free fatty acids, fatty acid derivatives (40–50 %), resin acids (20–25 %), and unsaponifiable (30–35 %) [8]. In appearance, it is a highly viscous liquid of dark brown color. The specifications of this product are shown in Table 1.

Wood pellets were also used in this work as a reference feedstock to compare the results obtained with the TOP. The elemental composition of the biomass and TOP are shown in Table 2. The table also includes the

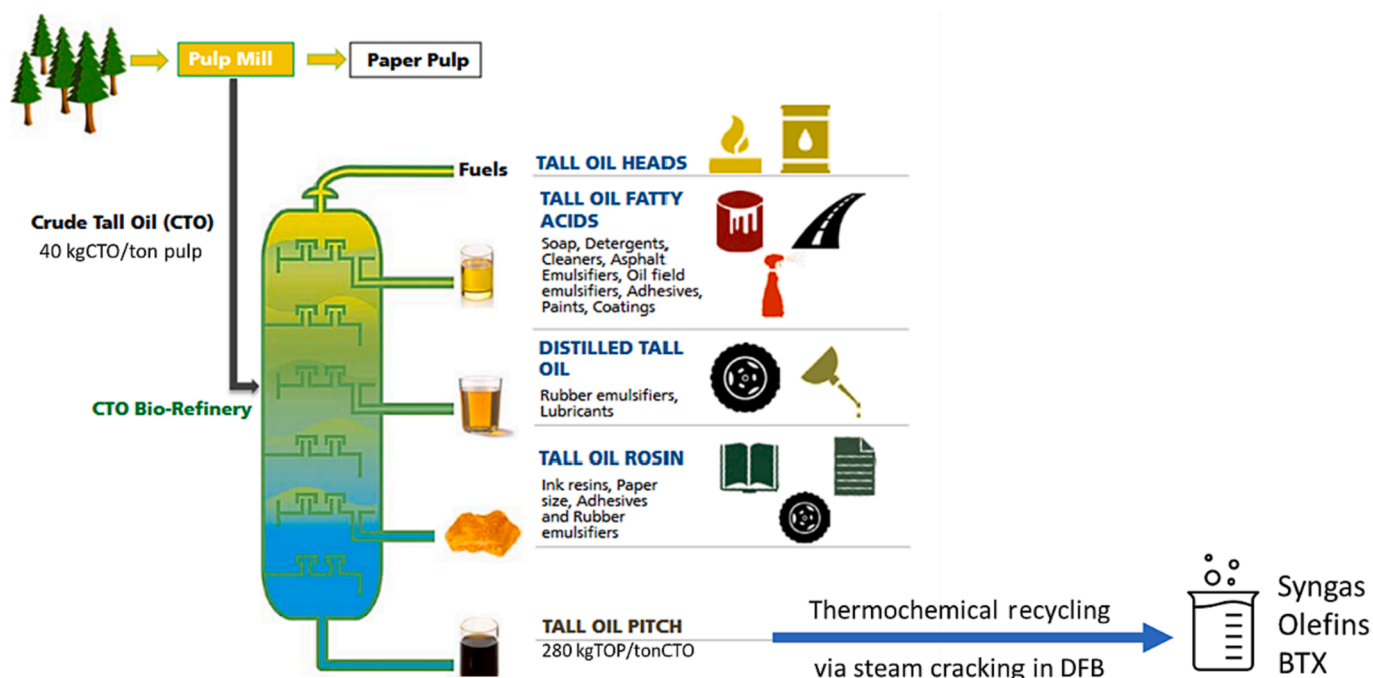


Fig. 1. Biorefinery cascading use of Crude Tall Oil (CTO) from kraft pulping (adapted from [3,4]). DFB: Dual Fluidized Bed, BTX: Benzene, Toluene, Xylene.

Table 1

Specifications of the tall oil pitch residue obtained after distillation of crude tall oil.

Parameter	Value
Flash point	243 °C
Relative density (20 °C)	1.0017 g/cm ³
Viscosity (100 °C)	30–45 mPa s
Acid number	75 mg KOH/g
Nitrogen content	40 mg/kg
Total Cl content	<1 mg/kg
High Calorific Value (HCV)	39.4 MJ/kg
Low Calorific Value (LCV)	37.1 MJ/kg

Table 2

Elemental composition of the wood pellets and TOP. Db: Dry basis.

Parameter	Wood pellets	TOP
C (% db)	50.1	80.3
H (% db)	6.2	11.1
O (% db)	43.0	8.4
N (% db)	0.06	≤0.01
S (%db)	0.22	≤0.02
Ash (% db)	0.4	0.18
Moisture (% wt.)	9.0	0.1
FC (%db)	16.0	1.1

fixed carbon content, obtained from a Thermogravimetric analyser (Leco, TGA701), using 1 g of fuel in a three-step process (drying, devolatilisation and fixed carbon combustion) with a temperature ramp of 50 °C/min.

2.2. Experimental set-up

The Chalmers dual fluidized bed (DFB) system was used in these experiments. This system consists of a 2–4-MW_{th} bubbling fluidized bed (BFB), coupled with a 12-MW_{th} circulating fluidized bed (CFB) combustor. A layout of the system can be seen in Fig. 2. In this figure, the different parts of the system are exposed. The path that the bed material

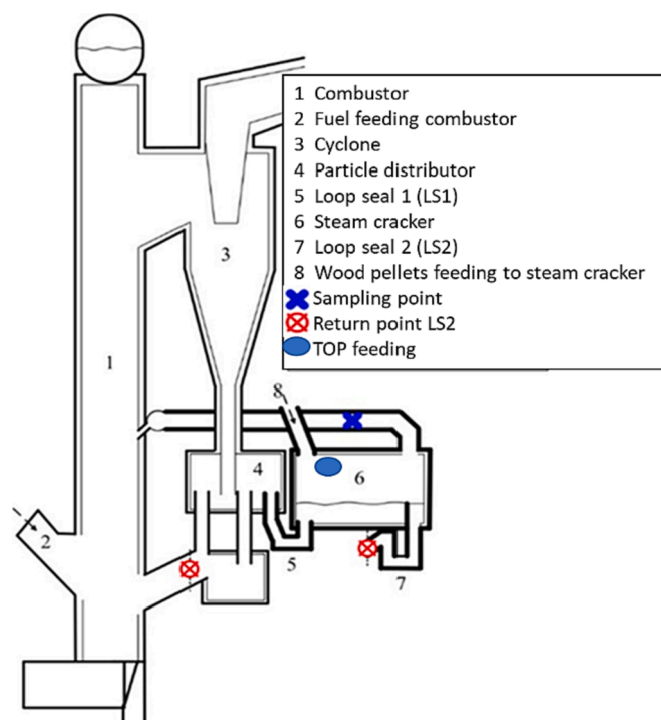


Fig. 2. Layout of the Chalmers Dual Fluidized Bed (DFB).

follows when circulating between the combustor (1) and the steam cracker (6) is described below. Coming from the combustor it is led to a cyclone (3) where the particulate matter is separated from the flue gas stream. The bed material is thereafter collected in a particle distributor (4), from where it can either be introduced into the steam cracker (6) or recirculated into the combustor. The bed material enters the cracker via a loop seal (5) and afterwards, it comes back to the combustor along with unconverted fuel, if any, through a second loop seal (7). Both the loop seals and the steam cracker are fluidized with steam preventing in this way leakages of flue gas and raw gas between both reactors. Since the purpose of this cracker is research, the raw gas produced in the cracker is fed into the combustor to generate additional heat. In a commercial process, the raw gas would continue to the gas cleaning and separation steps. To get more details of the operation of the Chalmers DFB system the reader is referred to the work of Larsson et al. [17].

The wood pellets was feed from the top of the steam reactor (8) a screw feeder. The TOP was pumped to the cracker through a heating line at 65°C, the flow was controlled via flow, pressure valves and to ensure stability the volumn and gas distribution of the products was continusly measured.

The experimental parameters used for both the wood pellets and the TOP are shown in Table 3, and all the experiments were performed the same day in the order shown in the Table. Here, the following parameters are exposed: the fuel flow to the steam cracker, the temperature, the flow of steam and the steam to fuel ratio (SFR). As can be seen, two reaction temperatures were selected to assess the effect of this parameter on the product distribution. Wood pellets were used as a reference case at high temperatures. In all cases, olivine was used as bed material and the bed circulation was kept constant. The gas residence time in the cracker was also maintained at 7 ± 0.5 s.

2.3. Gas measurements

A small flow of helium (20 L_N/min) was added to the steam cracker as a tracer gas to be able to quantify the total amount of dry raw gas produced per unit of feedstock. The raw gas produced during the process was continuously sampled from the sampling point (indicated with the blue cross in Fig. 2). This stream allows measuring the permanent gases and the aromatic hydrocarbons produced.

To quantify the permanent gas species, the raw gas was cooled down, quenched with isopropanol, and filtered, to remove water, aromatics and particles. Afterwards, it was analysed through gas chromatography. To this end, a micro-GC (Varian CP4900) was employed. This instrument was set and calibrated for He, H₂, CO₂, CO, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, O₂ and N₂.

The solid-phase adsorption (SPA) method was used to quantify the aromatics produced [18]. For an accurate measurement, at least 4 SPA samples were taken for each experimental case specified in Table 3. A GC-FID (Bruker GC-430) was used to identify and quantify the compounds with boiling points within those of benzene to coronene (C₆H₆ to C₁₈H₁₂). Twenty-eight aromatic compounds were calibrated, and the rest was estimated in relation to their mass (in all cases the estimated is less than 1 % of the aromatic content).

The carbon balance is studied to understand the product distribution

Table 3

Experimental parameters used during the steam cracking depending on the feedstock.

	Fuel flow, as received (kg/h)	T cracker (°C)	Steam flow (kg/h)	SFR
Wood pellets	300	825	160	0.53
TOP – 825 °C	150	825	160	1.07
TOP – 775 °C	175	775	160	0.91

and assess other unidentified compounds. The figure below shows the measured carbon-containing compounds with micro-GC (C1-C3) and with the SPA method (aromatics C₆-C₁₈). Biomass decomposition at the studied temperatures yields mostly the compounds covered by the analytic methods applied. In contrast, the high share of fatty acids in TOP is expected to yield a significant amount of linear hydrocarbons, in line with previous experiences with feedstocks that are rich in fatty acids, such as rapeseed oil [19]. Note that linear hydrocarbons with a carbon number larger than 3 fall out of the scope of the analytic methods applied. Based on the experience with rapeseed oil [19], such unidentified fraction may contain alkanes and cycloalkanes with carbon number C4-C5, i.e., H/C ratios between 2 and 2.5; and alkenes and cycloalkenes, i.e., H/C 1.5–2. In addition, PAH with a higher boiling point than chrysene (H/C < 0.67), here referred to as soot, can also be found in the products.

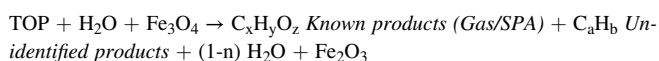
The share of the unidentified fraction in the total product distribution can be estimated by performing mass balances of carbon, hydrogen and oxygen. The carbon in the fuel is distributed as depicted in Fig. 3. For the hydrogen balance, the hydrogen in the dry product stream can originate both from the fuel and from the reacted steam. Similarly, the oxygen found in the dry product stream can come from the fuel and steam, but also from oxygen transfer from the bed material [20].

In this work, the unidentified fraction has been estimated based on the molar balances, i.e., by the difference between the C, in the feedstock and in the products measured. In addition, for the hydrogen content, a min/max has been estimated. The minimum is considering that the hydrogen in the dry product stream only comes from the fuel. In this case, any additional oxygen in the products should come from the bed material. The maximum hydrogen content of the products is estimated by considering that all hydrogen comes from reactions with steam. The reacted steam will also result in additional oxygen. Thus, the maximum hydrogen is calculated by the difference in oxygen in the products and the fuel input.

2.4. Energy balance

The energy balance aimed to determine the heat demand of the cracker when using TOP as fuel, and the heat output of a theoretical combustor that oxidizes the non-valuable products (here considered to be the PAH and C₄+ linear hydrocarbons), determined from the measurements and estimated from the molar balance. The aim is to investigate whether a cracker could operate without additional energy input to the combustor. The energy balance is based on [20–22]. The heat demand, heat output, sensible heat, and chemical energies are all presented in MJ/kg of fuel.

The heat demand (HD) in the steam cracker is the energy required to heat the reactants and products, as well as that needed to break and form chemical bonds. It was calculated using a balance of chemical and sensible energy, as described by Alamia et al. [21,22]. The simplified reaction is depicted below, where a fraction (n) of steam can react giving hydrogen and oxygen to the products. Alternatively, the additional oxygen in the products can come from oxygen in the bed, here represented as iron oxide, since the bed material was olivine.



The heat output (HO) is the heat produced in the combustor. It was

calculated given the LHV of the non-valuable products. Here, it was assumed that the non-valuable products are all those above C₄. The unidentified fraction contains hydrocarbons with carbon number C₄-C₅, thus, various LHV are possible according to the molar balances results. The lowest LHV among the possible products was taken to calculate the HO to obtain the minimum heat output.

3. Results and discussion

3.1. Gas and aromatic distribution

When the results obtained from the steam cracking of wood pellets are compared with those obtained from TOP, a clear difference is observed both in the gas and the aromatic yields. In Fig. 4, the molar yields of permanent gases are shown for the three cases investigated.

It can be seen that the steam cracking of wood pellets produces more carbon oxides and hydrogen than TOP steam cracking, while the trend for C₂-C₃ hydrocarbons is the opposite. On the one hand, the syngas produced from wood has a H₂/CO ratio of 2.6, which makes it appropriate for various synthesis processes, but the CO₂ concentrations are high. On the other hand, the syngas H₂/CO ratio of TOP is higher than 7, but a lower CO₂ yield is observed, which makes an overall H/C of the syngas (including CO₂) around 1, making it suitable for synthesis processes. In addition, the yields of ethylene and propylene measured for TOP were 5–7 times higher than the ones obtained from biomass.

The temperature plays an important role in decomposition. The results for TOP show that higher temperature leads to an increase in most of the gases produced (H₂, CO, CO₂, CH₄ and C₂H₄). In particular, at 825 °C the total gas yield is about 10 % higher than at 775 °C. The highest yield increase with temperature is observed in CO₂ and C₂H₄ (30 % and 20 % increase, respectively), while the yields of ethane and propylene show a 20 % decrease with the increment of temperature. If the aim is to recover syngas and ethylene, increasing the temperature promotes the recovery of those compounds.

Fig. 5 shows the aromatic yield obtained. When comparing the aromatic yields obtained with those derived from biomass, a clear difference can be observed. The total yield of hydrocarbons for the biomass was 13 g/kg fuel, whereas the yields for TOP were about 190 g/kg fuel.

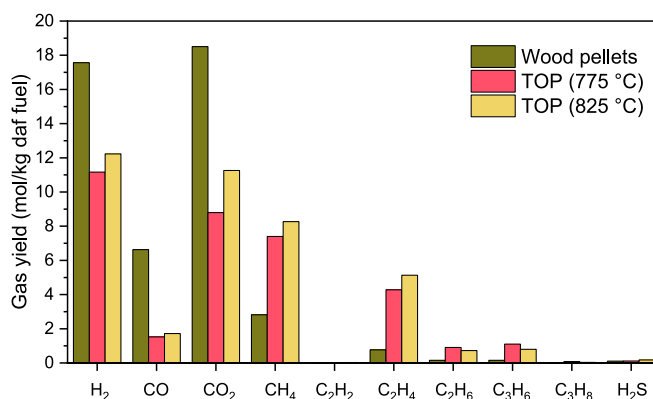


Fig. 4. Gas yield obtained through the steam cracking of tall oil pitch and wood pellets. In mol/kg of dry ash-free fuel.



Fig. 3. Carbon distribution of the products and its measurement technique.

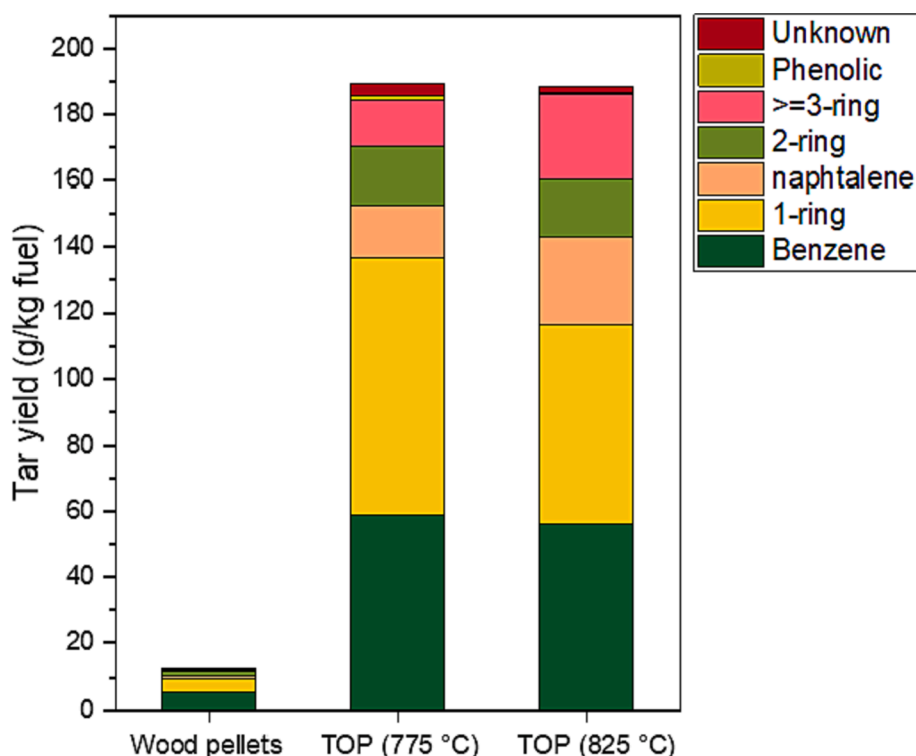


Fig. 5. Aromatic yield obtained via the steam cracking of Tall Oil Pitch (TOP) at 775C and 825C and wood pellets at 825C. Results are given in g/kg of fuel.

The main variations in aromatic yields with temperature correspond to the speciation rather than to the total yield. Increasing temperature results in an increase of naphthalene and the ≥ 3 -ring compounds decrease, while the yield of monoaromatics decreases.

A temperature of 775 °C seems to favour the production of base chemicals such as Benzene, Toluene and Xylene (BTX). BTX represent a share of 72 and 62 % of the total aromatic yield at 775 and 825 °C, respectively. Also, they represent an 11–13 %wt of the products, which is a significant amount that could be recovered to be used in the petrochemical industry.

3.2. Carbon balance

The carbon distribution of the products leaving the cracker is shown in Fig. 6, where 100 % corresponds to the total carbon in the feedstock used. The products are lumped into five categories: carbon oxides, methane, C_2 - C_3 hydrocarbons, BTX and polyaromatic compounds (PAH). The unidentified fraction is calculated by the difference between the carbon in the fuel and all carbon in the carbon-containing species identified (i.e., permanent gas and aromatic species).

The percentage of carbon in form of CO, CO₂ and CH₄, is more than

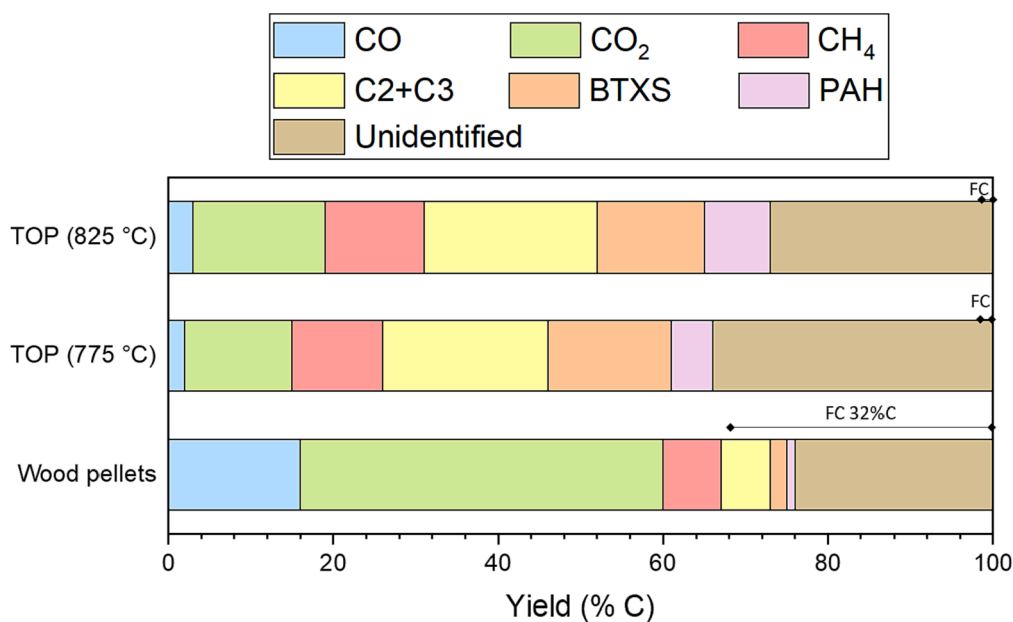


Fig. 6. Carbon distribution in the products obtained after the steam cracking of tall oil pitch and wood pellets. BTXS: Benzene, Toluene, Xylene; PAH: Polyaromatic hydrocarbons; FC: Fixed carbon. The FC is indicated with a line for reference and refers to the value obtained in the TGA.

double for wood pellets, 67 % of the carbon (%C), compared to TOP, which is 32 %C at the same temperature, 825 °C, and 26 %C at the low-temperature case. The main difference is the percentage of carbon in form of CO₂, which is significantly lower for TOP, 13 % and 17 % of the carbon for 775 and 825 °C, respectively, compared to wood, which is about 44 %C. This is the opposite for CO, where about 16 % of the carbon in wood products is in this form and only 2–3 %C for TOP. The methane content is lower for wood, 7 %C, and is 11–12 %C for TOP, reaching the lower end at 775 °C.

Concerning the olefinic products, C₂–C₃ fractions, TOP has a similar amount of carbon in this form 20–21 %C at the temperatures studied, while wood has only 6 %C at 825°C. A similar trend was observed for the aromatic fraction, TOP yields about 20–21 %C in aromatic compounds, while less than 3 %C for wood pellets. For both cases, BTX are the main compounds, having 2 %C, 13 %C and 15 %C for wood and TOP low and high temperature respectively. A low temperature seems to favour the conversion towards BTX, while higher temperatures seem to produce more PAH, i.e., 5 %C versus 8 %C. This denotes that increasing the temperature possibly led to polyaromatization [23,24].

A significant amount of carbon is unidentified. As shown in Fig. 6, the unidentified carbon content for the wood pellets case is 25 %. For TOP, the carbon contents are 26 % and 31 %C at high and low temperatures, respectively.

For wood pellets, the unidentified fraction is in the same order of magnitude as the fixed carbon content and a minor fraction of unidentified hydrocarbons is expected at the temperature applied in the experiment. The unidentified carbon content is 25 %, which is much lower than the fixed carbon obtained from the TGA, 32 %C. This indicates that there has been char gasification reaction to some extent, in line with previous investigations in the same unit and under similar conditions [14].

The TOP unidentified fraction was 25 %–31 %C, while the TOP fixed carbon is about 1 %C. Therefore, the contribution of the char to the unidentified fraction is minor. It can be expected that the unidentified fraction consists mainly of unmeasured hydrocarbon species and/or soot particles. This fraction can be unidentified hydrocarbons between C₄–C₆, linear and cyclic, that have a H/C ratio between 1.5 and 2.5. In addition, the unidentified compounds can also be PAH or soot with C > 18, which have a H/C from 0 to about 0.7. Thus, the hydrogen balance was investigated to get further insights into the content of the unidentified fraction.

Table 4 shows the estimated minimum and maximum hydrogen that can be found in the unidentified fraction. As explained in the method, the minimum hydrogen is estimated given that all the hydrogen in the fuel becomes a product and the maximum assuming all additional oxygen comes from steam. Thus, the H/C ratio of the unidentified fractions results between 0.7 and 2.1, at 775°C, and between 0.5 and 2.8 at 825°C. These ranges give a first impression of which compound may be present, but further analysis is needed to narrow down the possible hydrocarbons in the unidentified fraction.

For low temperature, previous research has shown a significant presence of C₄–C₆ linear hydrocarbons and low formation of soot. Mandviwala et al. showed 5 % of the carbon as C₄ hydrocarbon during steam cracking of rapeseed oil at 750 °C in a laboratory FB, and also 6 % of carbon not detected which is speculated to be C₅–C₆ hydrocarbons [19]. Given the fuel similarities of the rapeseed oil with TOP, both containing fatty acids, the presence of hydrocarbons between C₄–C₆, linear and cyclic, is likely. In addition, the range of H/C ratio of the

unidentified fraction ratifies that possibility, since it can reach up to 2.1. However, the lower minimum H/C ratio is 0.7, which indicates some soot may be formed. The same study showed <2 %C of soot formation at 750 °C compared to 5 %C of PAH. Therefore, it is probable that most of the unidentified products (32 %C) are cyclic and linear hydrocarbons between C₄–C₆, leading to a higher H/C ratio, and only a small amount of soot is formed during TOP decomposition at 775 °C. For instance, assuming 2 %C is soot, 30 %C will be cyclic and linear hydrocarbons between C₄–C₆.

For high temperature, the cracking severity increases, thus, decreasing the quantity of C₃ hydrocarbon in the products. Thus, it can be expected to have less linear hydrocarbons between C₄–C₆ than at 775 °C, as we have seen with the decrease of C₂H₆, and C₃H₆ when increasing temperature (Fig. 4). In other words, the presence of hydrocarbons between C₄–C₆ at 825 °C is possible but to a lesser extent than at 775 °C, which is also corroborated by the fact that less unidentified is found (26 %C at 825 °C compared to 32 %C, at 775 °C). When observing the H/C ratio, the theoretical maximum H/C ratio given by the hydrogen balance in Table 4 (i.e. H/C = 2.8) is unlikely not only due to an increase in cracking severity, and also given that the linear hydrocarbons have a H/C between 1.5 and 2.5. On the contrary, the minimum H/C is lower at high temperature than at low one, which points out towards a more pronounced soot formation. In addition, a growth of PAH was observed at 825 °C, thus, more soot was likely formed at a high temperature than at 775 °C. For instance, assuming 3–5 %C at 825 °C is soot, 21–23 %C will be cyclic and linear hydrocarbons between C₄–C₆, which is significantly lower than at 775 °C.

3.3. Energy balance

Table 4 also shows that the heat demand (HD) of the steam cracker is always lower than the heat output (HO) produced in the combustor. To calculate the energy balance, both HD of the steam cracker and the HO depend on the unidentified fraction, which in turn depends on the hydrogen balance. The table above depicts conservative estimates of the HD and HO, considering a minimum and maximum energy produced/needed. For the HO, the lower limit only includes the lowest energy of the estimated unidentified, while the upper limit also includes the PAH fraction. This choice results in a more conservative estimation of the heat balance and gives a more robust analysis of whether the process would need an external source of heat.

As can be seen, in both cases the heat output of TOP is higher than the heat demand, depending on the estimate. Thus, if both unidentified and PAH are combusted, the process will be self-sufficient and will not require additional energy, even, there is excess and lower temperature heat that could be used for other processes.

3.4. Recovery of valuable chemicals

TOP is a residue from the pulp industry that is nowadays burned producing heat. A possible alternative to avoid these emissions is to recover as much carbon as possible from this fraction in the form of valuable products. To evaluate the feasibility of doing carbon recycling of TOP waste, the steam cracking in a DFB system was investigated to recover the valuable chemical building blocks derived from this residue. As shown, around 35 % of the carbon (or 32–34 % in weight) of the TOP can be directly recovered as C₂–C₃ and BTX fractions which are valuable chemical building blocks. Compared to wood, this fraction is 4 times

Table 4
Hydrogen and energy balance. HD: heat demand and HO: heat output.

	Unidentified molC/ kgfuel (%C)	Min molH/kgfuel	Min molH/ kgfuel	Min H/C ratio unidentified	Max H/C ratio unidentified	HD (MJ/ kgfuel)	HO (MJ/ kgfuel)
TOP – 825 °C	16.9 (25%)	9.1	47.1	0.5	2.8	7.8–8.5	7.7–10.2
TOP – 775 °C	20.8 (31%)	14.3	42.1	0.7	2.1	7.0–8.0	9.6–11.2

more predominant in TOP.

While these valuable chemicals may be able to be recovered directly (after separation), the rest of the products need further treatment. The syngas produced can be sent to synthesis processes, given the adequate H₂/CO ratio [25,26]. In addition, CO₂ and CH₄ can also be included if followed by steam reforming and water gas shift reactions, but at the expense of using energy [10,14]. If such a synthesis process is in place, there is the possibility to additionally recover 67 %C from wood and 26–32 %C from TOP, via synthesis. However, it must be noted that wood produced more CO₂, thus, it requires more energy to be converted into chemicals [27].

If the gas, C₂-C₃ and BTX fractions are valorised, about 65 % of the carbon in TOP could be recovered. The rest of the products, PAH and unidentified fractions, are about 35 % for TOP. While some of the PAH and linear hydrocarbon could be recovered, like naphthalene, the rest will need to be treated. As shown, an option is to combust this fraction and employ the energy for the steam cracking process. Thus, combusting PAH and the linear hydrocarbon from the unidentified fractions is sufficient to run the process.

Today's combustion of TOP results in emissions of about 2.9 kg of CO₂ per kg of TOP. In Europe, about 180–240 k tons are produced annually [4,6], which results in about 530–700 k tons of CO₂ emitted due to combustion for energy recovery. If the valuable chemicals, C₂-C₃ and BTX, about 35 % of the carbon in TOP could be recovered, CO₂ emissions could be reduced by 185–245 k tons, without the need to use any additional energy source in the process. Although bio-based emissions can be considered neutral, the substitution of the fossil raw material used to produce those chemicals can reduce both fossil consumption and emissions, leading towards a circular bioeconomy.

4. Conclusion

In this work, the steam cracking of tall oil pitch residue was assessed as an alternative for the management of this residue from the pulp industry. Thermochemical recycling via steam cracking, in DFB at 775–825°C, can produce chemical building blocks that can be reintroduced into the chemical industry, therefore, leading to a circular use of the carbon atoms in the waste. About 35 % of the carbon in TOP could be directly recovered as C₂-C₃ and BTX fractions, and only 8 %C for wood pellets. In addition, the syngas produced seems suitable for the synthesis of other chemicals based on the H₂/CO ratio.

The effect of the reaction temperature was also assessed. Results showed that, within the operating window applied, the higher the temperature, the higher the fraction of valuable species that can be recovered, i.e. C₂-C₃ and BTX. The produced gases showed a higher yield when the temperature increased, but BTX compounds decreased. When compared to wood pellets yields, TOP steam cracking produced more light hydrocarbons (CH₄, C₂H₄, etc.), less syngas and beyond 10 times more aromatic compounds (190 g/kg of TOP vs 13 g/kg of biomass).

From the results obtained in this work, it can be concluded that TOP is an appealing option to consider as a source of reused carbon for the chemical industry leading to the circular use of this kind of residue. In addition, the process can be self-sufficient without additional energy sources.

CRedit authorship contribution statement

Isabel Cañete Vela: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Judith González-Arias:** Conceptualization, Writing – original draft, Writing – review & editing, Visualization. **Teresa Berdugo Vilches:** Investigation, Formal analysis, Validation, Writing – review & editing. **Martin Seemann:** Investigation, Supervision, Project administration, Writing – review & editing. **Henrik Thunman:** Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

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.

Data availability

Data will be made available on request.

References

- [1] Calvin K, Cowie A, Berndes G, Arneth A, Cherubini F, Portugal-Pereira J, et al. Bioenergy for climate change mitigation: Scale and sustainability. *GCB Bioenergy* 2021;13:1346–71. <https://doi.org/10.1111/GCBB.12863>.
- [2] Carus M, Dammer L. The “Circular Bioeconomy” – Concepts, Opportunities and Limitations - Renewable Carbon. Nova-Institut GmbH; 2018.
- [3] CTO n.d. <https://www.harrpa.eu/index.php/product-families/cto> (accessed September 27, 2022).
- [4] Venkat. Analysis of the European crude tall oil industry-environmental impact, socio-economic value & downstream potential Short Title: EU CTO-Added Value Study 2016.
- [5] Aryan V, Kraft A. The crude tall oil value chain: Global availability and the influence of regional energy policies. *J Clean Prod* 2021;280:124616. <https://doi.org/10.1016/j.jclepro.2020.124616>.
- [6] Cashman SA, Moran KM, Gaglione AG. Greenhouse gas and energy life cycle assessment of pine chemicals derived from crude tall oil and their substitutes. *J Ind Ecol* 2016;20:1108–21. <https://doi.org/10.1111/JIEC.12370>.
- [7] Narayan B, Hosokawa K, Miyashita M. Nutraceutical and specialty lipids and their co-products. *Nutraceutical and specialty lipids and their co-products* 2006: 201–218.
- [8] Holmbom B. Composition of tall oil pitch n.d.
- [9] Vela IC. Carbon materials: towards a circular economy through thermochemical recycling of mixed waste 2022.
- [10] Thunman H, Berdugo Vilches T, Seemann M, Maric J, Cañete Vela I, Pissot S, et al. Circular use of plastics-transformation of existing petrochemical clusters into thermochemical recycling plants with 100% plastics recovery. *Sustain Mater Technol* 2019;22:e00124.
- [11] Yang M, You F. Comparative techno-economic and environmental analysis of ethylene and propylene manufacturing from wet shale gas and naphtha. *Ind Eng Chem Res* 2017;56:4038–51. <https://doi.org/10.1021/ACS.IECR.7B00354>.
- [12] Zámotný P, Bělohav Z, Starkbaumová L, Patera J. Experimental study of hydrocarbon structure effects on the composition of its pyrolysis products. *J Anal Appl Pyrolysis* 2010;87:207–16. <https://doi.org/10.1016/j.jaap.2009.12.006>.
- [13] Arena U, Zaccariello L, Mastellone ML. Fluidized bed gasification of waste-derived fuels. *Waste Manag* 2010;30:1212–9. <https://doi.org/10.1016/j.wasman.2010.01.038>.
- [14] Pissot S, Vilches TB, Thunman H, Seemann M. Dual fluidized bed gasification configurations for carbon recovery from biomass. *Energy Fuel* 2020;34: 16187–200. <https://doi.org/10.1021/ACS.ENERGYFUELS.0C02781>.
- [15] Cañete Vela I, Maric J, Seemann M. Valorisation of textile waste via steam gasification in a fluidized bed reactor. *Proceedings - HERAKLION 2019 - 7th International Conference on Sustainable Solid Waste Management* 2019.
- [16] Berdugo Vilches T, Seemann M, Thunman H. Influence of in-bed catalysis by ash-coated olive on tar formation in steam gasification of biomass. *Energy Fuel* 2018; 32:9592–604. <https://doi.org/10.1021/ACS.ENERGYFUELS.8B02153>.
- [17] Larsson A, Seemann M, Neves D, Thunman H. Evaluation of performance of industrial-scale dual fluidized bed gasifiers using the chalmers 2–4-MWth gasifier. *Energy Fuel* 2013;27:6665–80. https://doi.org/10.1021/EF400981J/SUPPL_FILE/EF400981J_SI_001.PDF.
- [18] Israelsson M, Seemann M, Thunman H. Assessment of the solid-phase adsorption method for sampling biomass-derived tar in industrial environments. *Energy Fuel* 2013;27:7569–78. <https://doi.org/10.1021/EF401893J>.
- [19] Mandviwala C, González-Arias J, Seemann M, Martin, Berdugo Vilches T, Thunman H. Fluidized bed steam cracking of rapeseed oil: exploring the direct production of the molecular building blocks for the plastics industry. *Biomass Convers Biorefin* n.d.;1:3. doi: 10.1007/s13399-022-02925-z.
- [20] Pissot S, Berdugo Vilches T, Maric J, Cañete Vela I, Thunman H, Seemann M. Thermochemical recycling of automotive shredder residue by chemical-looping gasification using the generated ash as oxygen carrier. *Energy Fuels* 2019;acs. energyfuels.9b02607. doi: 10.1021/acs.energyfuels.9b02607.
- [21] Alamia A, Thunman H, Seemann M. Process simulation of dual fluidized bed gasifiers using experimental data. *Energy Fuel* 2016;30:4017–33. <https://doi.org/10.1021/ACS.ENERGYFUELS.6B00122>.
- [22] Alamia A, Larsson A, Breitholtz C, Thunman H. Performance of large-scale biomass gasifiers in a biorefinery, a state-of-the-art reference. *Int J Energy Res* 2017;41: 2001–19. <https://doi.org/10.1002/ER.3758>.
- [23] Onwudili JA, Insura N, Williams PT. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time. *J Anal Appl Pyrolysis* 2009;86:293–303. <https://doi.org/10.1016/J.JAAP.2009.07.008>.

- [24] Kaminsky W, Schlesselmann B, Simon CM. Thermal degradation of mixed plastic waste to aromatics and gas. *Polym Degrad Stab* 1996;53:189–97. [https://doi.org/10.1016/0141-3910\(96\)00087-0](https://doi.org/10.1016/0141-3910(96)00087-0).
- [25] Li S, Cañete Vela I, Järvinen M, Seemann M. Polyethylene terephthalate (PET) recycling via steam gasification – The effect of operating conditions on gas and tar composition. *Waste Manag* 2021;130:117–26. <https://doi.org/10.1016/J.WASMAN.2021.05.023>.
- [26] Zhao Z, Jiang J, Wang F. An economic analysis of twenty light olefin production pathways. *J Energy Chem* 2021;56:193–202. <https://doi.org/10.1016/J.JEACHEM.2020.04.021>.
- [27] Cañete Vela I, Berdugo Vilches T, Berndes G, Johnsson F, Thunman H. Co-recycling of natural and synthetic carbon materials for a sustainable circular economy. *J Clean Prod* 2022;365:132674. <https://doi.org/10.1016/J.JCLEPRO.2022.132674>.