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Technological Solution for the Sustainability of the Destructive Distillation of Wood in Classic Horizontal Retorts

S. Tomas,^{*} M. Planinić, A. Bucić-Kojić, M. Bilić, D. Velić, and M. Čačić Faculty of Food Technology, University of J.J. Strossmayer in Osijek, F. Kuhača 20, 31 000 Osijek, Croatia

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Dedicated to the memory of Professor Dr. Valentin Koloini

Charcoal production in retorts involves the pyrolysis i.e. thermal decomposition of wood in the absence of oxygen/air. The by products of this thermo-chemical process are tar, pyroligneous acid and wood gas. Pyroligneous acid can recover in several useful organic products by fraction distillation. However, the modern synthetic ways of their production are more economic, so that distillation of pyroligneous acid becomes irrational and is an abandoned procedure in "Factory of Wood Processing in Belišće". The factory in full capacity makes about 25 t of pyroligneous acid daily, which is recognised as an environmental pollutant and hence cannot be allowed to escape into streams. Therefore, to continue wood charcoal production it was necessary to dispose of pyroligneous acid in an environmentally friendly manner.

Four possible solutions to this problem were proposed. The innovative and acceptable solution found in the partial plant reconstruction that assumes direct combustion of exhaust retort gases instead of their condensation. The reconstruction gave several positive effects: the condensation phase was eliminated; retort gases became the main heating fuel that should provide ample heat for the plant; wastewater and gases are environmental-friendly.

Key words:

Charcoal, horizontal retort, pyroligenous acid, sustainable charcoal production

Introduction

Generally, there are global trends towards more sustainable production methods, waste minimisation, reducing pollution, conservation of natural resources, and reduction of greenhouse gas emissions.¹

Biomass can be converted directly into heat or can be subjected to conversion or refinement into an intermediate biofuel with some desirable properties such as better storage, ease of handling, greater convenience, compatibility with existing fuels, or higher energy density.¹ The conversion efficiency of wood as an energy source varies according to production systems.^{2,3}

Pyrolysis or carbonisation is a process for thermal conversion (decomposition) of wood and other solid fuels in the complete absence of an oxidizing agent (air/oxygen), or with such limited supply that gasification does not occur to any appreciable extent. During pyrolysis of lignocellulosic materials, most of the cellulose and hemicellulose as well as part of the lignin will disintegrate to form smaller and lighter molecules that are gases at the pyrolysis temperature, whereas the remaining part of biomass is left as a black porous solid and mainly consists of ligneous components.⁴ Various laboratory investigations^{5–8} of the thermal decomposition of wood have provided similar results. It can be concluded that the decomposition of different wood materials have qualitatively common behaviour and it is possible to distinguish four/five successive stages in the combustion process, corresponding to different temperature environments.

Apart from charcoal, liquid and gaseous products are produced if the charcoal is made in a retort by collecting them from the vapours driven off from retorts. The liquids are condensed when the hot retort vapours pass through water-cooled condenser and the condensate is called pyroligneous acid. Water is the main constituent ranging from 20 to 80 % depending on the moisture content of the wood being carbonised, and the stage in carbonisation at which the sample is collected. The other components comprise water-insoluble and water-soluble tar, acetic and related acids, methanol, acetone and small quantities of complex esters and similar compounds which may have uses in flavouring.

The non-condensable gases pass into condensers and are usually burned to recover the heat energy they contain. This wood gas, as it is called, is

^{*} Corresponding author. Tel.: +38531224335; fax: +38531207115; E-mail address: srecko.tomas@ptfos.hr

of low calorific value (around 10 % of that of natural gas). The products other than charcoal are usually referred to as by-products. Since the advent of the petrochemical industry, this by-product industry has become uneconomic because in most instances the chemicals can be produced from petroleum or synthetically more cheaply.

In Croatia, Belišće is the only industrial manufacturer of charcoal from wood mass, which is set up as a semi-continuous retort carbonisation system without subsequent recovery of pyroligneous acid. Charcoal production in full capacity (22.73 t of charcoal produced from 87.14 t wood wet weight or 65.52 t of dry matter of wood) gives about 25 t of pyroligneous acid per day, which is a highly polluting noxious corrosive liquid and hence cannot be allowed to escape into streams. Consequently, in order to continue this wood charcoal production, it was necessary to dispose of the by-products in an environmentally friendly way. This paper presents four possible solutions to this issue, which provide sustainable destructive distillation of wood in classic horizontal retorts. The proposed solutions are based on the example of the Belišće carbonisation plant.

The retort carbonisation system

The processing plant in Belišće (Fig. 1) constitutes six retorts that are approximately cylindrical in shape, each around 55 m³ in volume (R1-R6), two pre-drying chambers (DC1, DC2), which are out of use, and six charcoal cooling chambers



F i g. 1 - Scheme of the horizontal retort system for carbonisation in Belišće. (R1-6) retorts, (DC1-2) pre-drying chambers, (CC1-6) charcoal cooling chambers, (1) water-cooled condensers, (2) pyroligneous acid and tar vat, (3) scrubber for residual non-condensable wood gases, (4) scrubber gas stack, (5) flue gas stack.

(CC1-CC6). The wood is conveyed into steel wagons (two wagons per retort, one is 12 m³ in volume) that fit the dimensions of the retort rather closely to ensure maximum volumetric efficiency. The wagons roll into and are removed from the retort on steel rails connected to a cooling chamber of the same dimensions as the retort and built directly facing it, so that the wagons after carbonisation can be drawn quickly into the cooling chamber and sealed for cooling. Also, the trails and transfers connect the retorts with the wood storage yard located next to the retorts plant. Retorts are heated by an external heat source, i.e. by flue gases that occurr during combustion of natural gas and non-condensable wood gas with air, which flow through separated heated pipes at the bottom of the retorts underneath the wagons.

The wood gas is obtained by drawing off the gases and vapours from the retorts in the direction of lower pressure and passing the gas through water-cooled condensers (1) which condense first the tar and then the pyroligneous acid. The non-condensable gas passes through scrubber (3) and is fed to the burners underneath the retorts or is exhausted through the stack. The tar and pyroligneous acid is stored in a tank (2) to be separated later.

The usual raw materials are naturally dried roundwood, split roundwood, slabs from sawmilling and bark with average length of about 1 to 1.2 metres. The carbonisation stage takes about 24 hours and as soon as it is complete the retort is opened and the wagons drawn to the cooler which is then sealed to extinguish the charcoal which takes fire immediately as it is removed from the retort. Cooling takes from 24 to 48 hours depending on weather conditions and spreading of cooler walls with water.

Solutions for sustainable horizontal retort system of charcoal production

Solution I. The starting point of this solution was the fact that the 7 % of retort vapours and gas condensate are tarry substances, which can give heat by burning. The idea was to separate the tarry components from "pure" wastewater by condensation of retort vapours and gases in two steps, and by burning the non-condensable gases (Fig. 2). This separation is based on different boiling points (condensation temperature) of the gaseous product from the retorts.

Solution II. The aim of this proposal was also separation of tar, but based on the different densities of the individual compounds of the gaseous product from retorts, e.g. tar ($\rho \sim 1070 \text{ kg m}^{-3}$) and the rest of retort vapour and gas condensate



Fig. 2 – Schematic of tar component separation by two-step condensation of retort gas and vapour

($\rho \sim 1030 \text{ kg m}^{-3}$). Separation can be conducted by centrifugal force using continuous disc separators.

Solution III. This proposal provides a solution by burning pyroligneous acid in a combustion chamber (Fig. 3). It requires designing and building a new combustion chamber of adequate dimensions, which will ensure plenty of space for flue gas retention for at least 1 second. Pyroligneous acid will be heated, evaporated and burned with air in the chamber, producing flue gases of 900 °C. The hot flue gases will be cooled down to 400 °C by mixing with additive ambient air that will be introduced at the top of the combustion chamber. The cooled mixture can then be used as excess heat for other purposes in the process plant (e.g. drying of wood briquettes). Waste flue gases will be further cooled and exhausted into the atmosphere.



Fig. 3 – Schematic of the evaporation and combustion of pyroligneous acid for production of heat

Solution IV. This proposal (Fig. 4) provides an innovative solution for process redesign, which involves partial reconstruction of the existing process of destructive distillation of wood. The proposed innovation is based on the elimination of the retort gases and vapours condensation phase, as well as the scrubbing of the non-condensable phase. The complete mixture of retort gases and vapours is fed into the combustion chamber (1), because of their high heating power and the ability to produce flue gases with temperature of 900 °C, which can be used directly for wood biomass heating in the retorts. All the organic compounds in retort gases are flammable and the endproducts of this reaction are N_2 , O_2 , CO_2 and H_2O . Therefore, the oxygen can be used for their combustion, and the emission of waste gases to the atmosphere (2) is ecologically more acceptable than the original emission.



Fig. 4 – Schematic of the horizontal retort system for carbonisation with direct combustion of the retort gas mixture. (*R1-6*) retorts, (*DC1-2*) pre-drying chambers, (*CC1-6*) charcoal cooling chambers, (1) combustion chamber, (2) waste gas stacks.

After retort heating by the flue gases and their partial cooling, the flue gases are fed into the drying chambers (DC1, DC2) before they are released into the atmosphere. This way, all gas condesators and scrubbers in the carbonisation processes, as well as 22 burners and tubes for combustion gases can be eliminated, because the complete mixture of retort gases and vapours will be burned centrally in one combustion chamber. The 900 °C flue gases would be fed away by pipes positioned underneath the retorts and the drying chambers.

Wood carbonisation in horizontal retorts with direct combustion of the retort gas mixture instead of its condensation (Solution IV) is recognised as a potential solution that offers the most appropriate key to long-term sustainability. Finally, if the technological and economic analyses of the proposals listed above reveal their unsustainability, charcoal production process should be discontinued altogether.

Proposal analysis and optimal solution arbitrating

The proposed solutions I and II are based on theory. However, the pyroligneous acid consists of up to 100 different organic compounds and the main question is how to successfully separate the harmful compounds from the wastewater. The complete separation of all the wastewater organic compounds is impossible in an ecologically acceptable manner, because of their different boiling points.

Two-step condensation (Solution I) and centrifugation of pyroligneous acid (Solution II) cannot be used for adequate and complete separation of harmful components from wastewater.

The analysis of pyroligneous acid performed using GC/MC system in our laboratory detected a number of potentially harmful compounds, also confirmed by an analysis performed by the Alfa-Laval Company. For all the above reasons, proposals I and II were rejected as unacceptable. Proposed solutions III and IV, however, may result in ecologically acceptable processes, because both solutions involve the burning of pyroligneous acid by air in combustion chambers at 900 °C. Furthermore, it is important to choose the solution that is the most acceptable for industrial application. Further analysis is needed to make the decision, as well as detailed material and energy balances. Temperatures varied strongly, because the retorts batching is with phase delay (approximately four-hour delay). The given results of the performed analysis on retort gases and vapour is shown in Fig. 5.

Statistical calculation showed that the mean temperature of retort gases and vapours in all retorts was 346 °C, which is presented with a straight line



Fig. 5 – Temperature vs. time – measurements performed simultaneously in I-VI retorts

in Fig. 5. The mean temperature of the mixture of retort gases and vapours was around 275 °C, and that temperature was used for energy balance calculations concerning the proposed solutions III and IV.

When the carbonising plant works in full capacity, i.e. when all six retorts work as separate modules (at different carbonisation phase at the same time), the retort vapours and gases that are drawn from all the retorts and collected into a common channel are mixed together at around 275 °C. Each of the 6 retorts gets 2 wagons with 12 m³ of heaped log per wagon, which is around 7.8 m³ of wood mass per wagon. If the wood is a dried beech with 700 kg m⁻³ density, retorts are loaded with 65 520 kg of dry wood matter, and if the wood is naturally dried with 25 % moisture, the retorts have to evaporate 21 621.60 kg of water within 24 hours.

The stoichiometric equation of thermal decomposition of wood material^{9,10} (eq. 1) and mass balance enable qualitative/quantitative calculation of 24-hour charcoal production processes (Table 1).

Products		kg kmol ⁻¹	kmol d ⁻¹	x/% (φ/%)	kg d ⁻¹	w/%
wood charcoal	$C_{16}H_{10}O_2$	234	72.83	6.98	22 722.34	34.68
non-combustible gases and vapours	H_2O	18	679.84	65.12	16 314.48	24.90
	CO_2	44	121.40	11.63	7 122.02	10.87
combustible gases and vapours	СО	28	72.84	6.98	2 719.08	4.15
	CH ₃ COOH	60	48.56	4.65	3 885.34	5.93
	CH ₃ OH	32	24.28	2.33	1 035.22	1.58
	$C_{23}H_{22}O_4$	362	24.28	2.33	11 721.53	17.89

Table 1 – Composition and quantity of product of wood carbonisation

$$2C_{42}H_{60}O_{28} \rightarrow 3C_{16}H_{10}O_{2} + 28H_{2}O + 5CO_{2} + CH_{3}COOH + CH_{3}OH + C_{23}H_{22}O_{4}$$
(1)

The daily production is around ~ 22.7 t of charcoal and around 42.8 t of combustible and non-combustible gases and vapours which are retort by-products, whereof 45.23 % of mass is combustible, which is a considerable amount of potential gas fuel. According to theoretical energy balance, this kind of daily charcoal production requires ~ 170 GJ of heat.

Thus, the idea of this solution was to burn the mixture of gases and condensable from retorts as hot uncondensed gas as close as possible to the carbonising equipment. Therefore, it was necessary to calculate the lower heating value (net calorific value) of the retort gas mixture, as well as the composition and temperature of flue gases that occur during their combustion.

Combustion of certain combustible gases is carried out according to the following stoichiometric equations, eqs. (2–5):

$$CO + 0.5O_2 + 1.88N_2 \rightarrow CO_2 + 1.88N_2$$
 (2)

$$CH_{3}COOH + 2O_{2} + 7.52N_{2} \rightarrow$$

$$\rightarrow 2CO_{2} + 2H_{2}O + 7.52N_{2}$$
(3)

$$\begin{array}{l} CH_{3}OH + 1.5O_{2} + 5.64N_{2} \rightarrow \\ \rightarrow 2CO_{2} + 2H_{2}O + 7.52N_{2} \end{array}$$
(4)

$$C_{23}H_{22}O_4 + 26.5O_2 + 99.64N_2 \rightarrow \rightarrow 23CO_2 + 11H_2O + 99.64N_2$$
(5)

Total oxygen/air requirement for complete combustion of the retort gas mixture must comprise a theoretical combustion and theoretical (volume) excess ($\lambda_g = 1.15$) of combustion oxygen/air has to be added. This means that in order to ensure complete retort gas combustion, 172 t of dry air per day will be needed. Consequently, 216.5 t d⁻¹ of combustion gases will be produced, and this number will be enlarged for moisture immanent in ambient air.

The net calorific value of the retort gas mixture can be fairly accurately calculated according to eq. (6):

$$H_{\rm d} = 33900 \cdot c + 11700 \cdot \left(h - \frac{o}{8}\right) + + 10500 \cdot s - 2500 \cdot W \quad [\rm kJ \ kg^{-1}]$$
(6)

where the *c*, *h*, *o* and *s* are the mass fractions $[kg kg^{-1}]$ of carbon, hydrogen, oxygen and sulphur in gas, respectively, while *W* denotes the mass fraction of water in gas. Because retort gas does not

contain sulphur and the water is in the form of vapour, the net calorific value can be calculated according to eq. (7):

$$H_{\rm d} = 33900 \cdot c + 11700 \cdot \left(h - \frac{o}{8}\right) \, [\rm kJ \, kg^{-1}]$$
 (7)

and it is in the amount of 10.6 MJ kg⁻¹. This is the same amount of heat that will be released during the combustion of the retort gas mixture with air, and utilised to raise the temperature of flue gases. Thus, the temperature of the combustion gas can be estimated according to eq. (8), which represents the energy balance of the combustion chamber.

$$x_{a} \cdot [C_{p,a}]_{0}^{T_{0}} \cdot T_{a} + x_{rg,i} \cdot [C_{p,rg,i}]_{0}^{T_{rg}} \cdot T_{rg} + H_{d} =$$
$$= x_{fg,i} \cdot [C_{p,fg,i}]_{0}^{T_{fg}} \cdot T_{fg}$$
(8)

where $H_{\rm d}$ is the net calorific value of the retort gas mixture, x_{a} , $x_{rg,i}$, x_{fg} are the mole fractions [mol mol⁻¹] of air, retort gas mixture and combustion gas respectively, $C_{p,a}$, $C_{p,rg}$, $C_{p,fg}$ are related specific molar heat capacity and T_a , T_{rg} , T_{fg} are temperature of air, retort gas mixture and combustion gas. This kind of calculation gives the approximate temperature of flue gases of about 1400 °C. Together with the retort gas mixture and sufficient air needed for complete combustion, air has to be introduced into the combustion chamber for cooling of the combustion gas in amount of 6 kg air per kg of retort gas mixture. Thus, 473.5 t d⁻¹ of combustion gases at ~900 °C are released from the combustion chamber, which can be used for indirect heating of retorts. If the combustion gases are cooled down to 500 °C while going through the pipes underneath the retorts, they can give ~ 208.5 GJ d⁻¹ in total.

The above calculations justify the assumption that if all the retort vapour and gas products are burned without previous condensation (Solution IV), there would be ample heat to operate the retorts, but also a surplus for other purposes such as for drying wood in the pre-drying chambers. This gives additional benefit to the economy of the carbonisation process.

The balance calculation presented above is not possible for solution III, because the retort gases are cooled down from 275 °C to 20 °C. This results in latent heat loss of condensable compounds, and also sensible heat loss of all retorts gases and vapours from 275 °C to 20 °C.

For retort gas condensation and cooling from 275 °C to 20 °C the losses are around 98.5 GJ d⁻¹, given the average amount of latent heat of 2000 kJ kg⁻¹ and average specific heat of 3.80 kJ kg⁻¹ K⁻¹. The same amount of heat will be needed for vapourizing

the pyroligenous acid at the temperature of 275 °C, meaning that unnecessary heat of about 197 GJ d⁻¹ is spent (for solution III). On the other hand, the same amount of energy will be needed for heating the non-condensable gases. Further calculation shows that in this way the additional and unnecessary energy of 8.6 GJ d⁻¹ is spent. The sum of heat loss for solution III (compared to solution IV) is 205.6 GJ d⁻¹. This amount is equal to 6000 m³ d⁻¹ (at 293.15 K, 1 bar) of natural gases.

It is important to emphasize other possible benefits of the proposed solutions:

- Solution IV eliminates the condensation phase and retort gas scrubbing, which leads to the direct decrease in operational and service costs (for about 10 % of total costs);

- Solution IV, therefore, eliminates all condesors and scrubbers for gases in the processes, as well as 22 burners and tubes for combustion of natural gas because the complete mixture of retort gases and vapours will be burned in one central combustion chamber. Hot flue gases from the combustion chamber are fed into pipes underneath the retorts, thus indirectly pre-drying the wood biomass. This solution directly improves burning control, as well as total wood burning and decreases the heat loss, thus providing the possibility of automatic control of the heating processes in the retorts.

- Solution III proposes the burning of wood tar in a separate furnace, which means additional costs for its separation and manipulation. Even though the estimated investment costs for solutions III and IV are almost equal (~1 000 000.00 EUR), concerning all the above mentioned the advantage of solution IV is obvious. Further analysis of solution IV is needed in order to address the ecological issues.

In previous calculations of material and energy balances, it was evident that direct burning of retorts gas and vapour gives enough energy for heating the wood in the retorts, as well as for pre-drying processes. Natural gas is used only at the start-up of the carbonisation processes and for safety reasons.

– Evaluation of performances indicated that 90 % of total heat needed for wood carbonisation comes from burning the retort gases and vapour and only 10 % from natural gas burning.

All of the above indicates that possible payback time in the case of solution IV is 2.5 years, and "Belišće d.d." accepted this solution for process implementation.

Realisation step of accepted solution

The accepted solution IV was realised with the cooperation of: "Belišće d.d."; "Faculty of Food Technology Osijek"; "Classen Apparatebau Wiesloch GmbH", Deutschland and "Enerkon d.o.o.", Zagreb. Production started in mid 2005. In the four years of successful charcoal production using the redesigned processes, additionally set for measuring the relevant process parameters; the process controls and implementation of technical improvement was performed. The national legislation regarding the level of harmful substances in air was satisfied, since there is no production of pyroligneous acid. Also, heating of retorts was automated; consumption of heat energy for heating the retorts was decreased by about 70 %; productivity increased by about 20 %. Traditional production of high quality charcoal continues and 60 jobs have been saved.

Conclusion

All four proposed solutions were considered and priority was given to Solution IV.

Two-step condensation (Solution I) and separation by centrifugal force (Solution II) cannot be used for adequate and complete separation and isolation of harmful components from wastewater.

Combustion of pyroligneous acid (Solution III) is ecologically acceptable but from the economical point of view it is unreasonable because of significant dissipation of heat during condensation of vapours/gases by-products from the retorts and large energy requirement for re-heating of (previously condensed) pyroligneous acid.

Wood carbonisation in horizontal retorts with direct combustion of the retort gas mixture, instead of their condensation (Solution IV), is recognised as a potential solution that offers the most appropriate key for long-term sustainability. It is also a step toward the "ideal" carbonising process requiring no external heat to carry out the carbonisation.

Some economical and ecological advantages can be achieved with the proposed reconstruction of the carbonisation plant:

- No production of pyroligneous acid!, so the wastewater is free from hazardous components;

- Waste gases are more acceptable for the environment. Emission measuring was established in compliance with the Regulations on the Limit Values of Stationary Source Emissions to Air;

- Energy saving;

- Decreasing of operating costs;

Process time saving with pre-drying of wood mass;

All the above mentioned enables the sustainable production of high quality wood charcoal in a semi-continuous horizontal retort system.

Abbreviations

- CC cooling chambers
- DC drying chambers
- R retorts

List of symbols

- T temperature, K
- x mole fraction, mol mol⁻¹, %
- φ volume fraction, %
- w mass fraction, %
- C_n specific molar heat capacity, kJ kg⁻¹ K⁻¹
- ρ density, kg m⁻³
- c mass fraction of carbon, kg kg⁻¹, %
- h mass fraction of hydrogen, kg kg⁻¹, %
- $H_{\rm d}$ net calorific value, kJ kg⁻¹
- o mass fraction of oxygen, kg kg⁻¹, %
- s mass fraction of sulphur, kg kg⁻¹, %
- W mass fraction of water, kg kg⁻¹, %
- λ_{g} oxygen/air excess

Subscripts

- a air
- fg combustion gas
- rg retort gas mixture

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