GASEOUS EMISSIONS FROM THERMAL WOOD MODIFICATION AS A SOURCE FOR FINE CHEMICALS RECOVERY

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ABSTRACT: Heat treatment of wood in temperature ranges between 150-230 °C is used in order to modify certain wood properties without additional use of chemicals. Process emissions are burnt or washed from the off gases to make certain that no malodorous compounds are released. However, neither option can be considered sustainable. Our work aims at the characterization of these emissions, and in particular we are interested in the condensable gases emitted by an Austrian wood heat treatment plant. Emissions from 6 different wood types (spruce, fir, larch, oak, ash, robinia) were collected and analysed. A market survey of prices, availability and future demand for the compounds found most abundantly in the process emissions was conducted. Comparison of process design for emission recovery was carried out by review of the literature. The long term target of the presented work is to establish the liquid and gaseous emissions of wood heat treatment processes as a source for renewable and sustainable chemicals for the basic materials industry.
Keywords: chemicals from biomass, bulk chemicals, recovery of residues

1. INTRODUCTION

With regulations for environmentally safe wood preservation methods on the horizon, interest in alternative treatment technologies is growing steadily. Heat treatment of wood in temperature ranges higher than common drying temperatures (i.e. 150-230°C) has lately attracted the interest of research and industry. Within the last decade different heat treatment processes [1], [2] were developed all over Europe, which all aim at the modification of certain wood properties like controlled changing of colour, reduced shrinkage and swelling, improved rotting and fungal decay behaviour without additional use of chemicals. So far most of the research activities were mainly focused on process development and improvement, characterization of the properties of the treated wood and the understanding of the physico-chemical changes in the wooden material, to name some of the main topics.

Yet only little attention has been drawn to different environmental aspects of this process, e.g. to emissions arising during the treatment. Due to the early stage in development of the wood modification process, effective emission work-up procedures for this process have yet not been investigated upon. These emissions are nowadays treated in two different ways. Either they are burnt or a waste-gas scrubbing system is implemented to assure environmental safety of the process.

Emissions arising in the course of a heat treatment process have altogether not been investigated thoroughly. Released substances are not recovered at the present time, even though they make up for about 10% of the total dry mass loss of the treated wood. The mass loss during modification of wood is a result of complex chemical reactions and partial degradation of some wood constituents, mainly hemicelluloses. Cellulose and lignin are more resistant to chemical degradation [3]. The utilisation of the above mentioned organic emissions for different applications in the fields of chemistry, pharmacy or the timber industry itself seems very promising. Since there is no substantial quantitative data for process emissions available so far, our work aims at the characterisation of condensable gaseous emissions from a small sized Austrian wood heat treatment plant. We intended to identify potentially valuable compounds and quantify the available amounts for recovery. Market values for the most promising compounds are evaluated. First estimations for possible recovery processes and rough target values for economical viability of recovery processes will be presented and discussed.

2. APPROACH

The study was conducted in cooperation with an Austrian supplier for heat treated wood. Kiln capacity was app. 12 m³/treatment. 6 different wood types (spruce, fir, larch, oak, ash, robinia) were examined for specific emissions and total mass losses. Gaseous emissions from the process' only exhaust line were collected through a cooler (4°C)/cold trap (-50°C) combination. An average of 7 samples was taken during the coarse of each modification process (24-40h). A focus was put on the high temperature section of the process (130°C-200°C). Liquid aqueous samples were analysed for water content, pH and total organic carbon (TOC) content. After sample preparation (liquid/liquid- and solid phase extraction) qualitative and quantitative analyses of the organic compounds were carried out via GC/MS and GC/FID respectively. Total mass loss of treated wood-batch was monitored through simultaneous treatment of sample boards.

Market value of identified prospect compounds and process design for emission recovery was carried out by review of the literature.

3. SCIENTIFIC INNOVATION AND RELEVANCE

With a total production capacity in Europe of about 265,000 m³ in 2002 [4], emissions from wood heat treatment processes can be estimated at around 6,500 tons per year of organic compounds. The development of a sustainable solution for liquid and air emissions will not only benefit the environment but also enhance the overall profitability of a highly promising wood modification method. As a scientific innovation this work provides the foundations for new paths towards sustainable chemicals production for the basic material industry. The characterisation of emission compounds and evaluation of their potential economic value is supposed to initiate process redesigns towards closed loop processes including emission recovery within the timber industries.

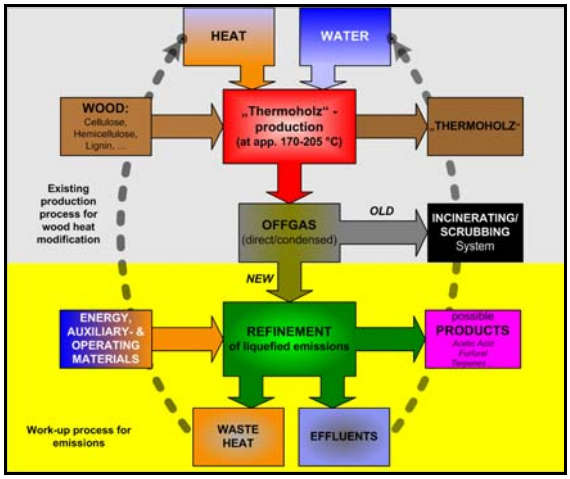

Figure 1: Simplified flow chart of wood heat treatment process and proposed changes

4. RESULTS

4.1. Emission Analyses

Emissions from 6 different wood types (spruce, fir, larch, oak, ash, robinia) were collected and analysed and specific mass losses of the heat treated timber were determined. Total mass loss (dry matter basis) varied from about 2 – 8% (fir, spruce: 2.6%; larch 4.6%; oak: 2.3%, robinia: 7,4%, ash: 7,8%). Table I shows a summary of average treatment conditions.

Table I: Average treatment conditions for different wood types

	max. temp. [°C]	mass loss [%]	avg. time [h]
Oak	170	2,3	24
Robinia	200	7,4	23
Ash	200	7,8	23
Larch	180	4,6	36
Fir	180	2,6	27
Spruce	180	2,6	28

pH values for all examined samples were in the range of 3,3 – 2,1 being a strong evidence for the significant amounts of short chain organic acids found in the samples. Both findings are in good accordance to the literature [5,6,7]. Figure 2 shows the amounts of total organic carbon found. The high TOC-values for ash and robina correspond well with their respective high total mass losses.

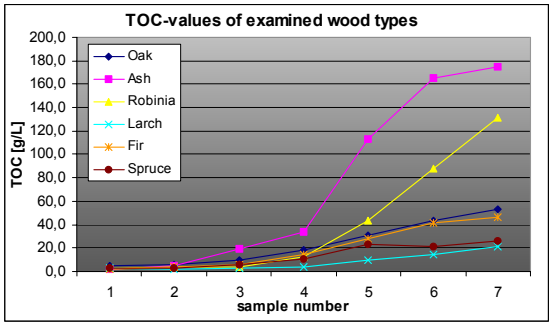

Figure 2: Total organic carbon contents of condensed emission samples, sample number corresponds with process stage

TOC-values also show, that with rising treatment temperatures the amount of emitted substances significantly grows, which is perfectly in line with data from literature.

In total, close to 100 different compounds were identified in qualitative analyses of emission samples, some of them however only tentatively. The most predominant compounds found throughout all samples were acetic acid, furfural and furfuryl-derivatives, making up for a total of about 80% of all identified compounds. Furthermore within the group of softwoods treated, emissions included significant amounts of mono-, sesqui-, and di-terpenes, mainly α- and β-pinene, δ-carene, limonen, α-terpineol, junipene, farnesene and resin acids such as abietic and dehydroabietic acid. The latter were also present in hardwood samples. Other identified compounds included: methanol, formic and propanoic acid, γ-butyrolactone, acetylpropionyl (2,3-pentanedione), 1-hydroxy-2-butanone as well as lignin derivatives like eugenol and iso-eugenol. Table II shows the total amounts of the quantified substances for the analysed wood types.

Table II: Summary of organic compounds emitted depending on treated wood types

Wood Type		Total organic compounds	Acetic acid	Furfural	Terpenes	mis. org. compounds
Oak	per batch [kg]	121,00	40,42	60,68		19,89
	per year [kg]	**2.904,00**	**970,14**	**1.456,44**	*n/a*	**477,42**
	[%]	100,00	33,41	50,15		16,44
Ash	per batch [kg]	423,00	278,90	86,79		57,31
	per year [kg]	**6.345,00**	**4.183,44**	**1.301,86**	*n/a*	**859,70**
	[%]	100,00	65,93	20,52		13,55
Larch	per batch [kg]	224,00	52,15	108,59	24,17	39,09
	per year [kg]	**5.152,00**	**1.199,50**	**2.497,51**	**555,93**	**899,06**
	[%]	100,00	23,28	48,48	10,79	17,45
Fir	per batch [kg]	101,00	21,50	40,76	9,75	28,99
	per year [kg]	**2.727,00**	**580,55**	**1.100,58**	**263,23**	**782,64**
	[%]	100,00	21,29	40,36	9,65	28,70
Robinia	per batch [kg]	432,00	233,04	127,59		71,37
	per year [kg]	**6.480,00**	**3.495,59**	**1.913,91**	*n/a*	**1.070,50**
	[%]	100,00	53,94	29,54		16,52
Total	**per year [kg]**	**23.608,00**	**10.429,22**	**8.270,30**	**819,16**	**4.089,32**
	[%]	100,00	44,18	35,03	3,47	17,32

4.2. Statistical Evaluation of Emission Data

A cluster analysis was performed on the obtained emission data. Cluster analysis is a multivariate analysis technique that seeks to organize information about variables so that relatively homogeneous groups, or "clusters," can be formed. Based on GC-FID results (all response factors assumed 1), the analysis was performed based on a semi quantitative definition level for the compounds found, i.e. “high content”, “medium content”, “low content”, “absent”. Measurement of distances is carried out by using the “city-block-distance” and the cluster-analytical results are based on the “nearest neighbour method”. Results indicate, that duration and maximum temperature of wood treatment not only strongly affect the amounts of emissions, but also the variety of substances emitted. Findings support the idea of fractionated collection of emissions occurring during the treatment process. Figures 3 show a dendrogram of high temperature treated robina. Other wood type emissions show similar results.

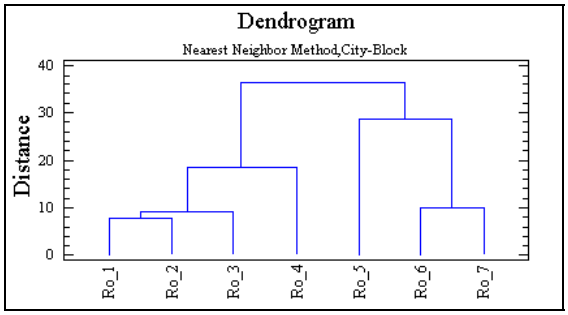

Figure 3: Cluster analysis of emissions from heat modified *Robinia pseudacacia*

4.3. Market Value of possible products

A market survey of prices, availability and future demand for the compounds found most abundantly in the process emissions was conducted. Moreover the substances' common applications were reviewed to estimate their prospective market opportunities. The goal was to determine whether a recovery process could prove economically viable at the moment within the given boundaries of small scale wood heat treatment operations in Austria. Table III gives an overview of some of the results. Stated market prices strongly depend on the purity of the chemicals, as is indicated by ranges given in Table III. Prices for fine and specialty chemicals are not stated, since fluctuations are very high and data is not very reliable.

Table III: Overview of prices for bulk chemicals recoverable from process emissions

Substances	*Market demand [10^3 t]*	*Current price [€/t]*	*Annual growth rate [%/yr]*
Acetic acid	2,567	170-190	+ 3 to 4
Furfural	225 - 275	700-1,700	n/a
Terpenes, pure	100	1,000-100,000	+ 5 to 8

In comparison, the crude emission solution (for further refinement) is estimated to be marketable at prices around 10 – 50 €/t.

4.4. Possible Recovery Processes

Within the pulp and paper industry recovery of valuable by-products is sometimes practised already (e.g. Lenzing AG, Austria, or [8]). The challenges there are similar to the examined process: a broad mixture of chemicals with only a few main components has to separated and most of the time extracted materials need further purification. As a first approach, common, suitable state of the art processes were studied for their possible employment on the case of the emissions of the wood heat treatment plant.

Generally speaking 4 main routes for by-products recovery were compared to another: Membrane separation techniques, extraction distillation and adsorption methods. Through a lack of data, adsorption methods were not included in the presented work. Main examination parameters were: possibility for utilisation in small scale process, costs of implementation, estimated operational costs and overall environmental performance of a redesigned process.

To summarise the results, no single process proved completely suitable for the recovery of emissions from wood heat treatment. Extractive methods would preferably be used for recovery of the bulk chemicals acetic acid and furfural. Membrane separation techniques would give high selectivity and therefore purity of the recovered substance. However, these techniques are relatively expensive, and hence not suited for small scales. Selective adsorption seems to be a viable option, but further research is need to answer questions on special adsorptive media. Distillation methods will be needed for purification of certain fractions, but will not work as an exclusive operation method. Yet there is no solution for utilisation of the entire stream of emissions, which is an important issue for the overall economics of the process as well as its environmental performance. At the moment non of the examined processes for recovery of emitted substances seems to be viable from an economical point of view.

5. CONCLUSIONS

Analysis of the emissions from a small-sized wood heat treatment plant in Austria was carried out in order to get more information on the possibility to recover substances emitted during the process. Emissions from 6 different wood types (spruce, fir, larch, oak, ash, robinia) were collected and analysed. Results obtained showed that decomposition of wood constituents strongly depend on temperature and time of treatment, as well as the wood type treated. Main components included: acetic acid, furfural and furfuryl derivatives. Furthermore significant amounts of terpenes were found in emissions from heat treated softwoods.

Market value of the examined compounds strongly depend on their purity and fields of application. Acetic acid and furfural are low priced bulk chemicals with a wide variety of applications. Terpenes, when pure, are valuable by-products but within highly fluctuating markets.

Recovery processes for identified chemicals have to fulfil many requirements in this special case of a small scale operation. 4 main process routes were examined, but no single route proved economically viable at the present time. Statistical evaluation of emission data indicates, that separated treatment of soft- and hardwoods as well as fractionated collection of emitted substances could favourably influence the economy of a future recovery process.

However our results show, that a broad range of potentially valuable chemical by-products is discarded without further utilisation. Our focus for future work will concentrate on the combination of possible work-up procedures as well as on the identification of further utilisation possibilities of crude emission liquids.

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