CHEMICAL ENGINEERING TRANSACTIONS
VOL. 88, 2021
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš

ISBN 978-88-95608-86-0; **ISSN** 2283-9216
DOI: 10.3303/CET2188183

Environmental Analysis of Hydrothermal Decomposition of Melamine Etherified Resin Fibre

Timotej Vidovič, Maja Čolnik, Mojca Škerget, Lidija Čuček, Damjan Krajnc, Jan Puhar, Annamaria Vujanović*

Faculty of Chemistry and Chemical Engineering, University of Maribor, Slovenia
annamaria.vujanovic@um.si

Plastic waste presents a significant problem for the environment as significant amounts of plastics are produced, of which the majority are still landfilled contaminating soils, waterways and aquifers. A particular challenge present thermoset plastic material, which are more difficult to recycle compared to thermoplastic materials. One of these thermoset materials are melamine resins, noted for their heat resistance and stable structure, but usually disposed in landfills after the end of their life cycle. Hydrothermal processes present a promising method to tackle the issue of reprocessing thermoset materials, as they utilize water at high temperature and pressure to convert plastic waste into useful materials.
Hydrothermal decomposition of melamine etherified resin (MER) fibres is studied in this work. The reaction occurs in a hydrothermal reactor with water at subcritical conditions. The aqueous phase extracted from the post reaction mixture was analysed using tube tests for the contents of formaldehyde, organic acid, total nitrogen, and ammonium. Environmental footprints are further analyzed based on the data obtained from experimental work, and compared regarding three different decomposition temperatures: 200, 300 and 350 °C. Footprint assessment is performed mainly using OpenLCA software and various databases. Environmental comparison of the processes is evaluated regarding to greenhouse gas (GHG), nitrogen, phosphorus, energy, and ecological footprints, and human toxicity potential. Results show that decomposition at 200 °C yielded the lowest environmental impacts. However, the highest amounts of secondary compounds were obtained when conducting the process at 300 °C.

1. Introduction

A rapid growth in plastic consumption has been seen worldwide in recent years which represents significant planetary threat due to plastic accumulation and pollution, affecting nearly all ecosystems globally (Borrelle et al., 2020). Plastics brought many advantages in various sectors, such as electronic, power, food, transport, health care, construction and other sectors supporting the modern society (Klemeš et al., 2021), but it also brought major problems. Large quantities of plastic waste leak into the environment and consequently causing not only significant environmental, but also economic damage (Shen et al., 2020).
There are many different types of plastic materials, which can be divided into thermoplastic and thermoset materials. Thermoplastic materials, such as e.g., polyethylene terephthalate (PET) can be re-melted which makes it easier to recycle. The main problem that comes with the recycling is the difficulty to automate the sorting of plastic waste and the energy required for the process (Ross and Evans, 2003). On the other hand, thermoset plastic materials cannot be remelted or reshaped (Filho et al., 2021), hence materials recycling is difficult or even could be impossible. This type of waste mainly ends up in landfills, which causes significant environmental burdens. Melamine resins are resistant thermoset plastic materials made from melamine, urea and formaldehyde by condensation polymerization (Maity and Singha, 2012).
Among promising methods to resolve the environmental plastic pollutions are hydrothermal processes which have a low impact on environment (Knez et al., 2018). To convert waste into materials, fuels and chemicals, water at high temperature and pressure is used as a main process medium. With the increase of temperature, the dielectric constant decreases, and the polarity of water changes from high polar solvent at ambient

Paper Received: 16 June 2021; Revised: 2 August 2021; Accepted: 4 October 2021
Please cite this article as: Vidovič T., Čolnik M., Škerget M., Čuček L., Krajnc D., Puhar J., Vujanović A., 2021, Environmental Analysis of Hydrothermal Decomposition of Melamine Etherified Resin Fibre, Chemical Engineering Transactions, 88, 1099-1104 DOI:10.3303/CET2188183

conditions to a non-polar solvent at subcritical conditions (Čolnik et al., 2021b). With the hydrothermal decomposition under mild conditions liquid products with lower molecular weight (alcohols, aldehydes, carboxylic acids, esters etc.) are formed from solid waste (Bayat et al., 2021).
Some studies have investigated recycling opportunities of melamine formaldehyde waste. It could be used for lightweight concrete production (Chaitongrat and Siwadamrongpong, 2018), as flame-retardant filler for polyurethane foam (Wang et al., 2019), and in other applications. Several studies have also dealt with hydrothermal processing of waste plastics to produce valuable materials (Shen, 2020). However, to the authors' best knowledge, there have been no studies of hydrothermal processing of melamine etherified resin (MER) fibres, while also no evaluations of hydrothermal processing have been performed from an environmental perspective.
The main goals of this study are to investigate the decomposition of MER fibres at different temperatures and perform environmental assessment of the decomposition process at different temperatures. Hydrothermal decomposition is a promising technology for decomposing MER fibres, which are organic-based non-woven materials containing a 1,3,5-triazine skeleton. The decomposition behaviour at different temperatures was investigated, placing the investigated temperatures around the triazine decomposition temperatures. A conceptual Life Cycle Assessment (LCA) approach is used to assess the environmental impacts of the process.

2. Hydrothermal Decomposition of Melamine Etherified Resin Fibres

In this section preparation of used sample and chemicals is described. First, the process of breaking down MER fibres using hydrothermal decomposition is explained, and further the analysis of aqueous phase after the decomposition is presented. The aqueous phase was analysed using tube tests for formaldehyde, total nitrogen, ammonium and organic acids.

2.1 Process description

First, MER fibres were prepared for hydrothermal decomposition. MER fibres are advanced thermoset technical textile materials which are fire-resistant and do not shrink, melt or drip. MER fibres are produced from formaldehyde, urea, ammonia, and melamine resin and have a structure of a triazine ring. They contain over 50 wt.% of nitrogen, 35 wt.% of carbon, and remaining amounts of oxygen and hydrogen. The microscopic view of MER fibres is shown in Figure 1. To improve the overall exposure of MER fibres, they were cut into smaller pieces of 1 cm x 1 cm.

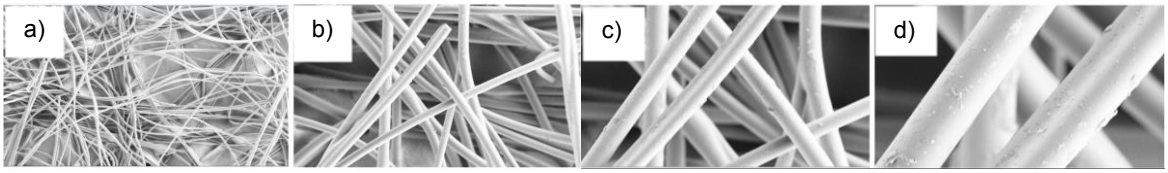

Figure 1: Microscopic view of MER fibres at: a) 200x, b) 1000x, c) 2000x and d) 5000x magnification

For the decomposition of MER fibre, a 75 mL high pressure, high temperature batch reactor (series 4740 Stainless Steel, Parr Instruments, Moline, IL, USA) was used, which is designed to withstand the maximum operating temperature of 540 °C and pressure up to 580 bar (Čolnik et al., 2021a). The experimental set up used for hydrothermal decomposition is shown in Figure 2.
Decomposition of MER fibres in subcritical water was conducted at three different temperatures (200, 300, 350 °C) for 1 h. First, the reactor vessel was filled with 0.5 g of MER fibre and 20 mL of deionized water. Further, it was flushed three times with inert gas N_2, and then filled up with N_2 so that the pressure of the reactor would be set to 20 bar. The reactor was then heated up to the desired temperature and decomposition was conducted for 1 h, at that temperature which was maintained with a heat-insulating tape made of glass wool and a heating coil.
At the end of degradation, the reactor vessel was cooled down to room temperature with cold water. The aqueous and solid phases were further separated using a centrifuge. In this study, the aqueous phase of the reactor solution was further analysed.

2.2 Analysis of aqueous phase

The aqueous phase of the reactor solution obtained from the decomposition was analysed using NANOCOLOR tube tests. The contents of formaldehyde, total nitrogen (TN_b), ammonium (NH_4^+, NH_3 and NH_4-N) and organic acids were determined. The used measuring ranges and applied methods of individual NANOCOLOR tube tests are shown in Table 1 (Macherey Nagel, 2021).

Figure 2: Experimental setup for hydrothermal decomposition of MER fibres in subcritical conditions

Table 1: Measuring range and applied methods of tube tests

Parameter	Measuring range	Method
Formaldehyde	0.1-8.0 mg/L HCHO	Chromotropic acid
Total nitrogen (TN_b)	0.5-22.0 mg/L N	2,6-Dimethylphenol
Ammonium	0.04-2.30 mg/L NH_4-N	Indophenol
	0.05-3.00 mg/L NH_4^+	
Organic acid	30-3,000 mg/L CH_3COOH	Ethylenglycole/Iron(III) ions
	0.5-50.0 mmol/L CH_3COOH	

To obtain the required measuring range of individual parameters, the aqueous phase was diluted accordingly with deionized water. Tube test analysis was performed in duplicate, and an average value was calculated and presented in Figure 3 which shows the results for the content of a) formaldehyde, total nitrogen (TN_b), b) organic acids and c) ammonium in the forms of ammonium ion (NH_4^+), ammonia (NH_3) and ammonium-nitrogen (NH_4-N) in the aqueous phase of reactor solution. Error bar in Figure 3 indicates standard deviation among the duplicate measurements. For clarity, the TN_b content value is presented as $TN_b \cdot 0.1$, which means that the value shown must be multiplied by 10 to obtain the measured value.
Figure 3a) shows that the higher values for formaldehyde content were obtained at reaction temperature of 200 °C (0.7±0.1 g/L) and the lowest at 300 °C ($0.9 \cdot 10^{-3}$ g/L). The higher TN_b content was obtained at 300 °C (7.0 ±0.8. g/L), while the lowest TN_b content at 200 °C (2.4±0.1 g/L). Figure 3b) shows that similar trend as for TN_b is obtained, the highest amounts of organic acids were found in the sample that took place at 300 °C (910±2.5 g/L), and the lowest at 200 °C (34.8±1.8 g/L). For ammonium, the highest value was determined in the reaction that took place at 300 °C (2.6±0.06 g/L for NH_4^+, 3.06 g/L for NH_3 and 2,6±0.06 g/L for NH_4-N) as shown in Figure 3c). The lowest values of ammonium were obtained at 200 °C ($0.09 \pm 3.1 \cdot 10^{-3}$ g/L for NH_4^+, $0.12 \pm 3.1 \cdot 10^{-3}$ g/L for NH_3 and $0.09 \pm 3.1 \cdot 10^{-3}$ g/L for NH_4-N). At 300 °C, the highest values of measured compounds were obtained, except the formaldehyde. Much higher values of formaldehyde were found in case of reaction taking place at 200 °C than at other two temperatures. Conceptual LCA was then performed evaluating all the inputs and the measured outputs in the aqueous phase.

3. Life Cycle Analysis

To evaluate the environmental aspect of hydrothermal decomposition for converting MER fibres into secondary raw materials, conceptual LCA was performed. The process at various temperatures was evaluated on the basis of five different environmental impact categories: greenhouse gas (GHG), phosphorus, nitrogen, energy, and ecological footprint, as well as human toxicity potential. The LCA study was performed in coherence with ISO 14040 series (International Organization for Standardization, 2006a, b). OpenLCA 1.10.3 (GreenDelta, 2020) software with the integrated Ecoinvent 3.6 database (Ecoinvent Version 3.6, 2019) was used to conduct the analysis.
Functional unit considered in the LCA analysis was 1 g of decomposed MER fibres. The data was based mostly on experimental work. The input and output data associated with the hydrothermal decomposition process at the reactor's operating temperatures of 200, 300 and 350 °C was compiled in Life Cycle Inventory (LCI) tables, which are presented in Table 2. Inputs required for the process are liquid nitrogen and deionised water which do not differ with operating temperature, and electricity consumption which is increasing with increased

temperature. The input data for MER fibres was taken from available databases, and it considers a production process which includes production of formaldehyde and melamine required to synthesise MER fibres. Formaldehyde is assumed to be produced from methanol via gasification of coal, Formaldehyde is assumed to be produced from methanol via gasification of coal, while melamine utilizes ammonia production and later, urea production. The outputs consist of the produced organic acid, as well as excess ammonium, nitrogen, and formaldehyde, which are released into the environment. The current Slovenian electricity mix was considered in the analysis. LCA was conducted as a cradle-to-gate analysis, with the system boundaries represented by production of input chemicals from raw materials and the products obtained in the reactor solution.

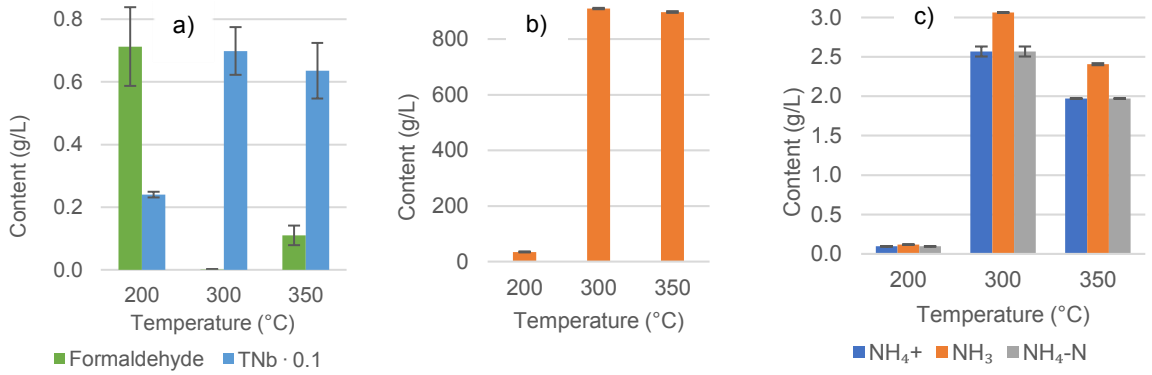

Figure 3: Tube test results for a) formaldehyde and total nitrogen, b) organic acids and c) ammonium content

Table 2: Life Cycle Inventory data for hydrothermal decomposition of MER fibres at various temperatures

Parameter	Amount (200 °C)	Amount (300 °C)	Amount (350 °C)	Unit
Inputs				
MER fibres	1.0	1.0	1.0	g
Nitrogen	$8.9 \cdot 10^{-3}$	$8.9 \cdot 10^{-3}$	$8.9 \cdot 10^{-3}$	g
Water	40	40	40	g
Electricity	0.3	0.4	0.4	kWh
Outputs				
Ammonium	$3.8 \cdot 10^{-3}$	0.1	$7.9 \cdot 10^{-2}$	g
Nitrogen	0.1	0.3	0.3	g
Formaldehyde	$2.9 \cdot 10^{-2}$	$3.6 \cdot 10^{-5}$	$4.4 \cdot 10^{-3}$	g
Organic acids	1.4	36.4	35.9	g

4. Results

The results for the five environmental footprints and human toxicity potential are presented in Figure 4. Energy footprint scale was modified to better fit the graph, and the value shown must be multiplied by 100 to obtain energy footprint value in GJ. Various units for each footprint category can be found in the literature, and the most typical units are used in this work, which are mass units for GHG, phosphorus and nitrogen footprints, and energy units for energy footprint. Ecological footprint was evaluated based on the average contributions of land occupation, nuclear energy use and CO_2 emissions from fossil energy use (Huijbregts et al., 2007), all of which are represented in the graph. Due to potential health risks due to formaldehyde exposure, additionally human toxicity potential is evaluated.

Results show that all footprint categories with the exception of nitrogen footprint increase similarly according to the increased reaction temperature. As temperature is increased from 200 °C to 300 °C, an increase roughly between 33 % and 36 % is noticed in the selected footprint categories. Furthermore, when temperature is increased from 200 °C to 350 °C, the increase in selected footprint categories amounts to roughly 38 % to 42 %. This increase is also present in all the impact categories which contribute to the ecological footprint (CO_2 emissions, nuclear energy, and land occupation). A similar trend as for ecological footprint was observed by using other methods for ecological evaluation such as the Sustainable Process Index (SPIonWeb, 2013). Larger increases are noted in the case of nitrogen footprint, as it is increased by 83 % at operating temperature of 300 °C and by around 88 % at operating temperature of 350 °C.

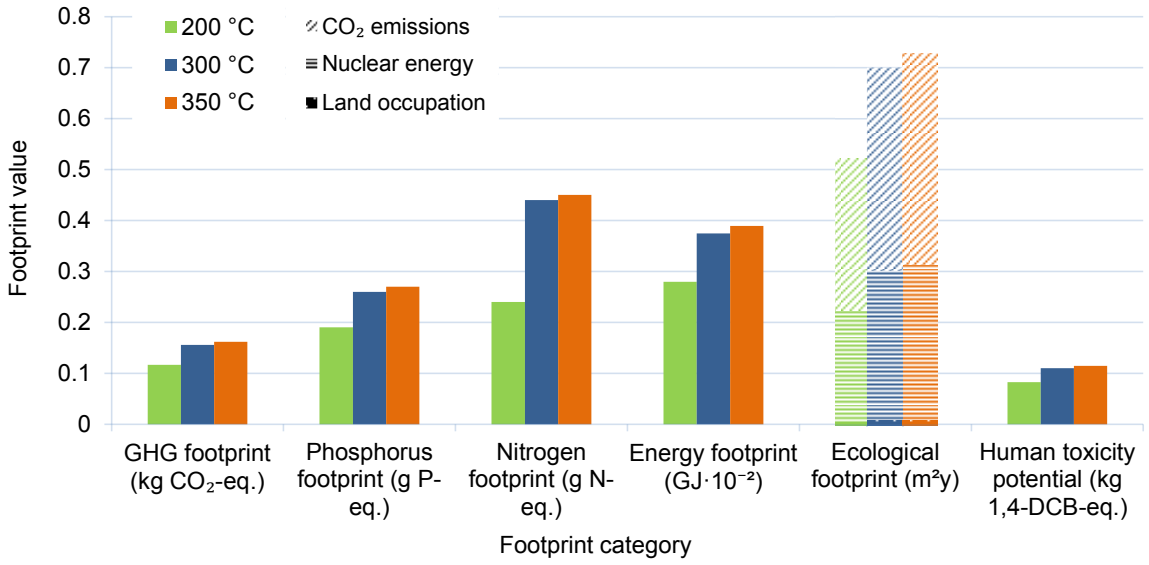

Figure 4: LCA analysis results for hydrothermal decomposition of MER fibres at various temperatures

In terms of contribution to the environmental impacts, electricity is found to have by far the most significant impact. The contributing percentage of electricity is between 95 to 99 % for all environmental footprints and potential environmental impacts except for nitrogen footprint, where its contribution is around 42 % for the process at 200 °C and around 56 % for the process at 350 °C. This is mainly due to consideration of the Slovenian electricity mix, where a substantial amount is provided by thermal energy from coal. The other contribution to the environmental impacts comes from MER fibre production, where most of the energy demand comes from heating required for ammonia production. Regarding life cycle phases, the manufacturing phase for MER fibres is the most significant contributor to the environmental impact. As the demand for electricity increases with increased temperature, the contribution of electricity to environmental impacts also increases.

5. Conclusions

In this paper, three different alternatives (reaction temperatures) for hydrothermal decomposition of MER fibers were investigated. In the analysis of aqueous phase of reactor solution with the use of tube tests, the reaction that took place at 300 °C yielded the highest values of ammonium, organic acids and total nitrogen and the lowest value of formaldehyde. The highest amounts of formaldehyde were determined in the reaction that took place at 200 °C. The possible cause for lower values of formaldehyde at 300 °C and 350 °C can be because of the thermal decomposition of triazine rings that occur at around 300 °C. At 200 °C, the triazine rings do not yet decompose and so more of the whole samples remain intact, but when the temperature is raised up to 275 °C and above, the ring disintegrates and more of the sample decomposes.

An environmental assessment of the process at different temperatures was conducted, using five environmental footprints (GHG, nitrogen, phosphorus, energy and ecological) and human toxicity potential. The process at 200 °C showed the best environmental performance in all the categories assessed. The results show that the process at increased temperature corresponds to an increase in environmental impacts. The results can be attributed to a higher demand for electricity with increased reactor temperature.

Despite the optimal environmental performance of the first scenario at 200 °C, from a technological standpoint, the second scenario at 300 °C presents results where the highest amount of secondary compounds are obtained. These results correspond to the decomposition of the triazine rings at around 275 °C, which means that optimal results for hydrothermal decomposition can only be achieved above this point.

An important limitation of this work is that the experiment was performed on a laboratory scale, where only tube tests were used to evaluate produced compounds and only the aqueous phase was analyzed. Therefore, this is a conceptual LCA assessment. For an estimate of the LCA results once the process is scaled from lab to industrial scale, a scale-up framework (Piccino et al., 2016) could be used. As electricity consumption of the reactor might be reduced with scaling up the process (Čolnik et al., 2021a), comparatively lower environmental impacts could be expected compared to the smaller laboratory scale.

Data quality assessment will be performed in the future to assess the reliability of tube tests. In the future, analytical methods will also be developed to ensure a more detailed analysis of both the aqueous and gaseous phases, as well as to identify other compounds present in the reactor solution. The area of hydrothermal decomposition temperature will also be explored in more details to consider the various criteria and find the optimal decomposition temperature.

Acknowledgements

The authors would like to acknowledge financial support from the Ministry of Education, Science and Sport of Republic of Slovenia (project No. 5442-1/2018/106) and the Slovenian Research Agency (research core funding No. P2-0412 and project N2-0138). Authors would also like to acknowledge help and support from Olivija Plohl for conducting SEM analysis on the inlet material.

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