# Furniture wood waste depollution through hydrolysis under pressurized water steam: Experimental work and kinetic modelization

Maximilien Gibier, Mohammad Sadeghisadeghabad, Pierre Girods, André Zoulalian, Yann Rogaume

Title: Furniture wood waste depollution through hydrolysis under pressurized water steam: Experimental work and kinetic modelization

Maximilien GIBIER, Mohammad SADEGHISADEGHABAD, Pierre GIRODS, André ZOULALIAN, Yann ROGAUME.

Université de Lorraine, INRAE, LERMAB, ERBE, F - 88 000 EPINAL, France

Abstract:

As the Recycling of wood waste becomes more important each year, wood products that contain urea-formaldehyde resins gained more attention due to the release of formaldehyde and other chemicals which have a critical impact on humans health and the environment. In this study, the hydrolysis of wood wastes from a French furniture industry was studied under different controlled conditions (temperature/pressure, steam ratio). An original on-line method to measure the emission of formaldehyde and ammonia using a FTIR spectrometer and a dilution system was applied successfully in this study. The effect of operatory conditions on formaldehyde and ammonia released is discussed. A mathematical model was also introduced to model the behavior of the ammonia and formaldehyde emission in the hydrolysis of wood waste.

**Keywords:**

Wood waste remediation, Urea-formaldehyde resin, hydrolysis, FTIR on-line measurement, Kinetic modelisation

Environmental Implication:

This paper is focused on the hydrolysis process used to remove pollutants from wood waste, namely from the furniture sector. Such waste contains high quantities of resins, namely urea-formaldehyde resins which contains nitrogen and are responsible for Nox emissions during its valorization by combustion or of formaldehyde and ammonia if the landfilling is preferred. This work aim therefore to develop a depollution process using no chemical reagent and being as energy efficient as possible to favor the use of end-life wood as raw material for different industrial sectors such as wood panel boards (Insulation panels, MDF, particleboard, …).

# 1. Introduction

Renewable energy is undoubtedly the most suitable approach to the challenges caused by fossil fuels. As a significant part of the biomass, wood is the focus of many studies. Wood has several advantages regarding the bio-economy concept. Wood as a natural material offers many outstanding characteristics in thermal conductivity and mechanical strength, which expands its use into many areas. Its consumption has increased from the beginning of the last century for different new applications (Bernstein et al., 2016) such as energy production, building materials, chemicals, etc. At the same time, wood waste consumption from end-of-life wood-based products is increasing. Wood waste contains additives and pollutants (resins, paints, preservatives, heavy metals, etc.) and contaminating materials (metals, plastics, glass, stocks, etc.), making recycling wood waste much more complicated than raw wood (Besserer et al., 2021).

Wood waste-based matters from products at their end-life show a notable amount of material to be valued in agreement with EC Waste Directive 2008/98. The construction, destruction, and aged furniture waste that holds many wood-based agglomerates, are the main waste streams in the European Union (Ihnát et al., 2017). In France in 2018, the furniture industry as a great source of agglomerated wood waste materials such as particleboards (PBs), produced almost 2 million tons of pieces of furniture which half ended up landfilled (Waste furniture sector France report, 2020). Today, the wood waste management strategy is mainly based on disposal (landfill and incineration), energy recovery, and material recovery (Lykidis and Grigoriou, 2008).

Even if the material recovery way is much more complicated than others, it appears to be the best way for various reasons; it allows extending carbon storage in matters, which could slow down its release in $CO_2$ form at end-life energy recovery (Lubke et al., 2020). This large amount of material could also constitute an abundant and inexpensive source of raw matter for new materials production while limiting economic stress on the wood industrial field caused by increased wood consumption (Besserer et al., 2021).

The main contaminant of furniture waste wood, especially PBs and MDF (medium density fiberboard), is the resin used as glue. The most common resin is urea-formaldehyde (UF) resin (Irle et al., 2010). Indeed, UF glue presents many advantages with a low cost, a high chemical reactivity (short polymerization duration), and an absence of color after polymerization (Liu et al., 2018; Irle et al., 2010). Unlike other waste wood contaminants (plastics, metals, glass) which could be sorted automatically, adjuvants like resin could not be easily eliminated (Ren et al., 2022). It is therefore essential to find a way to "clean up" such a waste before using it as new raw material for recycling.

Two ways have been identified to remove UF resin from wood waste. The first one is the pyrolysis process conducted in low severity conditions (between 250 and 300°C for some minutes). In different studies, it was shown that low-temperature pyrolysis (<350°C) could remove up to 70% of the nitrogen in PBs (Girods, 2008; Girods et al., 2008, 2009a, 2009b), in which the nitrogen content was used as resin content indicator knowing that natural nitrogen content in wood is very low (<0.1%) (Cowling and Merrill, 1966). Low-temperature pyrolysis mixed with combustion was also suggested (Jiang et al., 2010). This approach was could be insufficient since ammonia might still be converted to nitrogen oxides during the combustion step in oxygen-rich circumstances.

The second way identified is based on one of the weaknesses of UF resin, namely its sensibility to water which limits, therefore, its use in outdoor applications (Irle et al., 2010). It is known that the presence of moisture can make the UF polymer chain go through a hydrolysis reaction (i.e., the chemical mechanism described in Fig. 1) which leads to shorter polymer pieces and aggravates the mechanical properties of the wood-UF composite (Besserer et al., 2021).

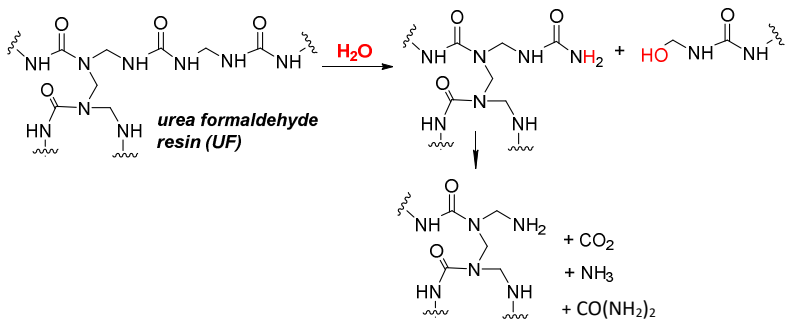



Figure 1. Prolysis of urea—formaldehyde resin (adapted from Hagel and Saake, 2020)

The susceptibility of UF-based adhesives to hydrolysis can be used in favor of recycling wood-based PBs that use these adhesives as glue in their structure.

The condensation and hydrolysis reactions of UF resin are largely described in the literature (Samaržija-Jovanović et al., 2011; Myers, 1986; Myers, 1982; Pizzi and Mittal, 2003). The hydrolysis reaction of UF resin leads mainly to forming formaldehyde, urea and intermediate compounds (resin fragments) of various molecular weights (Lubis et al., 2018). According to Myers and Koutsky (1990), the hydrolysis of all the bonds of the UF resin leads to the release of formaldehyde, with the exception of the C=O carbonyl and C-N amide bond. The works of Wan et al. (2014) and Hagel et al. (2020) showed an increase in pH is linked to the presence of ammonium ions in the water, which suggests the production of ammonia following the hydrolysis of the UF resin polymers.
Steam cooking can be used to separate the UF resin from the wood fibers in wood wastes by hydrolysis in a pressurized saturated steam environment (Lubis et al., 2018). It has been shown that the hydrolysis of cured resins is strongly affected by the pH of the medium in the following order acid > neutral > alkali. The optimum conditions to eliminate UF resin from MDF were found to be 80°C for 2 hours in the presence of oxalic acid (Lubis et al., 2018). Compared to acidic conditions, pure steam treatments are less expensive due to the use of less corrosive materials, and there is no need for a separation step, which makes the process more environmentally friendly (Hagel et al., 2020). Another study also showed that this hydrolysis reaction could be facilitated by treatment at higher temperatures using water steam. In the study, water steam at temperatures of 150–190°C for 10–20 minutes removed almost 80% of the resins (Wan et al., 2014). Different approaches have been tried to approximate the stability of UF resins facing hydrolysis by testing the formaldehyde release and structural stability (Park et al., 2013; Ringena et al., 2006).

Among all the information, it could be stated that literature is rich concerning the hydrolysis process used to “clean up” wood waste contaminated by UF resin. In literature, studies on this concept have been performed mainly in the liquid phase, using chemical agents. In addition, no possible on-line monitoring of the depollution of UF has been proposed. To our knowledge, no articles deal with neither the on-line measurement of emissions during the hydrolysis nor the kinetics of such a curing process.

It is therefore proposed in this work to investigate hydrolysis as an efficient method for the depollution of wood waste under steam pressure at lab scale in batch mode. The effect of the couple pressure/temperature and the steam ratio on the efficiency and the kinetics of the reaction has been studied. Gas emissions are on-line measured through FTIR spectrometer analysis to follow in real-time the decomposition products of UF resin. HPLC measurements on liquids and Kjeldahl on solid phases are performed to confirm FTIR measurements. Finally, a kinetic model based on a simplified chemical mechanism is proposed to allow the prediction of gas emissions according to steam curing operatory conditions. This last point is essential to supply reliable information for scaling such a process at the industrial scale.

# 2. Materials and methods

## 2.1 Wood wastes

The crushed wood waste was supplied by VALDELIA (A French eco-organism that ensures the collection of professional waste furniture). The waste is crushed by their sorting center, allowing a relatively homogeneous mixture. The particle size of the wood waste supplied ranges from 0 to 30 mm. After the reception, the wood waste is first sorted using a mechanical sieve, equipped with a 1cm×1cm sieve in order to remove fine particles as well as metal pieces manually.

The composition of the waste batch used in our study (about 4m$^3$) is evaluated on the content of 2kg of wood waste: 42% of raw wood, 51% of particleboard and 7% of fiberboard. No MDF was identified in this batch of wood waste.

It was decided to choose actual waste coming from landfill and not from new panels in order to simulate properly the use of waste. Indeed, their storage in landfill (wet and outdoor conditions, micro-organisms) can lead to the beginning of glues degradation (Lee et al., 2014). The proportion of waste contaminated by melamine-formaldehyde and phenol-formaldehyde resins is therefore unknown. The nitrogen content on a dry basis was measured at 2.5%.

Wood waste was dried in stainless steel bins in an oven at 103°C for 7 days before the steam cooking experiments to get rid of unstability of moisture of waste with time and to assume a better control of the inlet waste sample mass. Moisture content after the drying step was assumed to be inferior to 2%.

## 2.2 Kjeldahl analysis

Kjeldahl analysis is a relatively simple method for determining nitrogen of various nitrogen compounds such as amines and quaternary ammonium salts. It does not allow the direct dosage of nitrates, nitrites, nitrosyls, and cyanides, which must first be reduced to ammonia (Hepburn, 1908). The Kjeldahl method was performed in three steps of mineralization, distillation, and titration (Hepburn, 1908). The mineralization process was performed in a BUCHI Speed Digester K-436. Titration was afterward performed using a digital pH meter (Titroline easy, Schott, Mainz, Germany).

Kjeldahl was used to evaluate the mass of nitrogen removed by comparing the mass of nitrogen in the solid sample before and after the experiment. Assuming that the mass loss of waste is negligible during the test (loss of mass not determinable on the device), the mass of nitrogen removed can then be calculated.

## 2.3 HPLC method

High-Performance Liquid Chromatography (HPLC) was used to quantify the formaldehyde in liquid samples, a well-known method available in the literature (Ihnát et al., 2017; Li et al., 2007; Nishikawa and Sakai, 1995; Wahed et al., 2016; Xu et al., 2011). The HPLC measurement was performed on a ThermoFischer UltiMate 3000, equipped with an Acquity UPLC BEH C18 column, with a particle size of 1.7 µm (50mm x 2.1mm id.). Separation was achieved using a mixture of water/acetonitrile (60:40, v/v between 0-4 min - 10:90, v/v between 4-6min - 60:40, v/v between 6-10min). The total run time was 10 min. The flow rate was 0.3 mL/min and the injection volume was 1 µL.

The formaldehyde contained in the sample requires a derivatization step to be quantified by HPLC. The pH of the sample is first adjusted to 5. 1 mL of solution is taken and centrifuged for 10 min at 12,000 rpm. The sample is then filtered with a syringe and a 45µm diameter nylon filter. 20 µL of the sample was placed in a 1.5 ml glass vial with 30µL of DNPH solution (derivatization reagent) and 1 mL of acetonitrile (disperser). The sample was mixed using a Vortex-mixer and stored for HPLC analysis. The HPLC software automatically calculates the amount of formaldehyde measured in the sample by comparing the area obtained with the area of a 2µg/ml standard solution.

## 2.4 FTIR measurements

HPLC and Kjeldahl methods determine depollution process efficiency, but they are off-line and quantitative analysis. That is why an on-line qualitative and quantitative measurement method has been developed to characterize hydrolysis products of wood waste and follow the kinetic of pollutants devolatilization. Infrared spectrometry has been chosen for these analyzes since it allows fast, qualitative and quantitative analysis of the gas phase. Since gas effluents of the hydrolysis process mainly consist of water steam (more than 99 vol.%) and because of a high sensibility and a large adsorption band of water with Infrared spectrometry, a dilution system (dilution in nitrogen with a ratio close to 100x) has been added.

The infrared spectrometer (FTIR) used was a GASMET DX-4000 FTIR multi-component gas analyzer (Temet Instruments OY, Finland), a portable FTIR gas analyzer. The resolution of the obtained spectra was 8 $cm^{-1}$. The device was used to measure the ammonia and formaldehyde emissions during hydrolysis. The calibration of the FTIR spectrometer was obtained on pure water steam after dilution in nitrogen.

Formaldehyde calibration curves were established by vaporization of liquid solutions with concentrations from 250 to 8000 mg/L under steam atmosphere (between 2250 $cm^{-1}$ and 2850 $cm^{-1}$). Ammonia calibration curves were established using ammonia gas tanks with different concentrations of 500, 1000, and 5000 ppm under nitrogen atmosphere (between 910 $cm^{-1}$ and 1150 $cm^{-1}$). All calibrations were performed using the dilution system to avoid any error in the dilution ratio.

## 2.5 Steam-cooking pilot (depollution by hydrolysis at lab-scale in batch mode)

The steam cooking pilot used to perform the experiments is a combination of different apparatuses (steam generator, reactor, furnace, and condensation system). The steam generator could produce and maintain pressure up to 8 bars inside the reactor. The reactor is an inox 2.5-liter volume vessel, which is placed inside an oven. A schematic view of the steam cooking pilot is presented in Fig. 2.

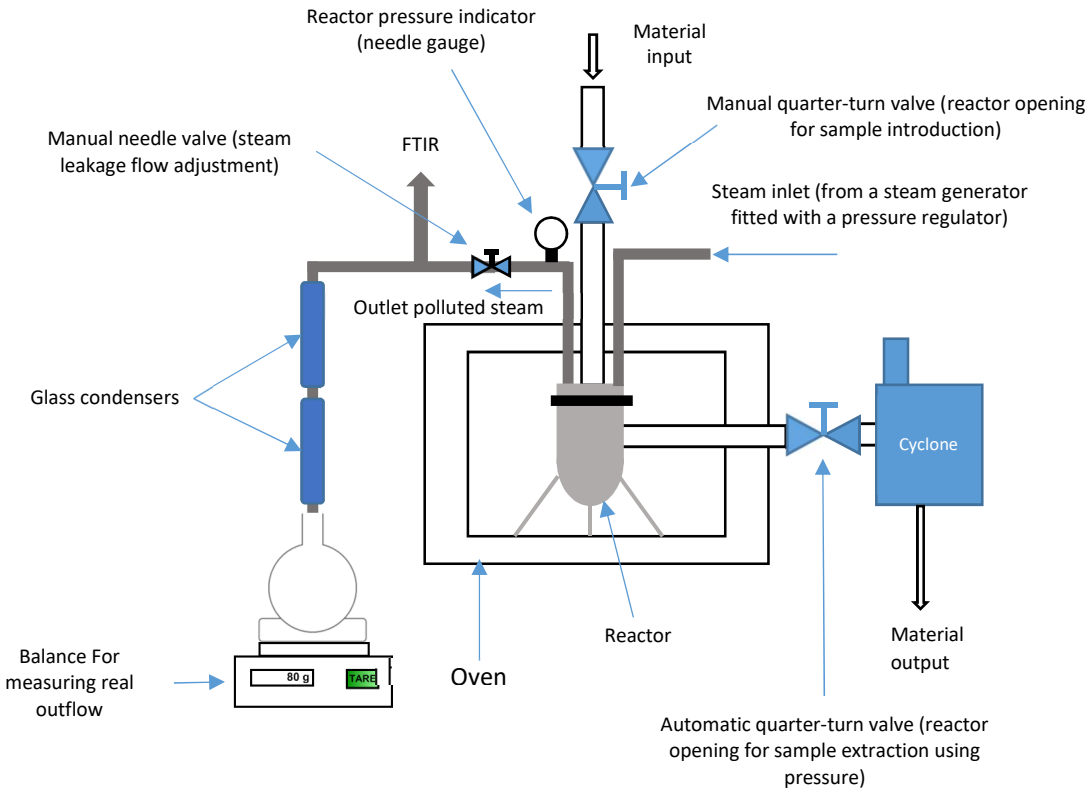


Figure 2. Steam cooking apparatuses schematic view

Inlet samples were introduced through the head of the reactor via a feed line. A manual quarter-turn valve allowed the opening and closing of the supply line. For the extraction of the treated materials, an automated quarter-turn valve made it possible to open the reactor via a horizontal pipe through which the treated materials, under pressure, escaped and were collected at the base of the cyclone which ensures the solid/vapor separation.

The reactor was supplied with steam (produced by a steam generator fitted with a pressure regulator), and the pressure was measured using a needle gauge. In order to analyze on-line the hydrolysis products, a steam leakage flow is controlled through a needle valve. The steam flow allows also to evaluate the effect of the steam ratio which is given as the ratio between steam flow and the mass of waste sample used for the test ($g_{steam}$/min/$g_{wood\ waste}$). A condensation system composed of two coolers in series supplied with cold water by a high-power cryostat (Unichiller 022-H-MPC with a maximum power of 3335W) is positioned at the outlet of the polluted steam flow line. The condensed liquid was then collected in a container weighed by a scale connected to a computer which calculates and records continuously instant steam flow rate. The condensation system thus designed allows a maximum condensation flow rate of 30 $g_{steam}$/min.

A tiny part of the polluted vapors is automatically sampled to feed the gas measurement device (dilution system + FTIR spectrometer). This sampling flow is assumed largely lower than the steam leakage one, ensuring a good steam leakage flow measurement. The gases leaving the reactor consists mainly of water vapor (not far from 99%) which makes it impossible for the on-line gas analysis by FTIR measurement (.due to the broad band of water adsorption in the infra-Red). This is why a dilution system was used to dilute the gas to be analyzed (dilution rate close to 100). Preliminary tests have shown the effectiveness of the method.

Regarding the dosage of formaldehyde, quantifications were also carried out by HPLC on the liquid phase collected to verify the accuracy of the measurement by IRTF. Concerning the one ammonia, nitrogen balance was performed by measuring nitrogen content in solids before and after experiments.

Two parameters were tested during the experiments: The temperature/pressure couple and the steam ratio ($g_{steam}$/min/$g_{waste}$). Regarding the temperature-pressure couple, the temperature of the oven was always set at a few degrees above the dew temperature (according to steam pressure) to avoid any condensation of the steam in the reactor and, therefore to work under dry steam.

## 2.6 Tested conditions

Tests in different conditions were performed to evaluate the effects of pressure/temperature couple as well as steam ratio. Close to all tests were performed with 40g of waste sample. Because of the limitation of steam leakage flow at 30 $g_{steam}$/min, tests for 1.5 and 3 $g_{steam}$/min/$g_{waste}$ steam ratios were carried out with lower sample mass. The duration of each run was 1 hour. Tests were triplicated and the average results are presented here. All tested conditions are summarized in table 1.

Table 1. Different conditions tested during the experiments

| | Pressure (bar) | Temperature | Wood waste | steam flow | Steam ratio |
|---|---|---|---|---|---|

| | | (°C) | dry mass (g) | ($g_{steam}$/min) | ($g_{steam}$/min/$g_{waste}$) |
|---|---|---|---|---|---|
| **Effect of temperature** | 2.5 | 139 | 40 | 30 | 0.75 |
| | 3.5 | 148 | 40 | 30 | 0.75 |
| | 4.5 | 155.5 | 40 | 30 | 0.75 |
| | 5.5 | 162 | 40 | 30 | 0.75 |
| | 6.5 | 168 | 40 | 30 | 0.75 |
| **Effect of steam ratio** | 3.5 | 148 | 40 | 10 | 0.25 |
| | 3.5 | 148 | 40 | 20 | 0.5 |
| | 3.5 | 148 | 40 | 30 | 0.75 |
| | 3.5 | 148 | 20 | 30 | 1.5 |
| | 3.5 | 148 | 10 | 30 | 3 |

# 3. Results and discussion

## 3.1. Hydrolysis products characterization by on-line FTIR measurement

Fig. 3. shows the typical absorbance spectrum obtained by FTIR during the hydrolysis of wood waste during steam cooking. It appears that only three species are produced during degradation, at least in detectable quantities: carbon dioxide (double peak at 2650 $cm^{-1}$), ammonia (double peak at 950 $cm^{-1}$), and formaldehyde (around 2800 $cm^{-1}$). This is consistent with the literature (Wan et al., 2014; Hagel et al., 2020; Park et al., 2013; Ringena et al., 2006). Hagel et al. (2020) also reported the production of acids (acetic and formic), but their presence in the gas phase was not identified. It could be due to their too low concentration or to the fact that being less volatile than ammonia and formaldehyde, these compounds stay in a liquid state in these conditions.

Peaks corresponding to water vapor appear in negative (3500-4000 $cm^{-1}$ and 1400-1800 $cm^{-1}$). This point is expected because, in order to avoid the saturation of the water vapor response (present in a large majority in front of the other species), the blank (reference measurement) was carried out under pure water vapor (after dilution). The presence of the other constituents under test conditions, therefore, reduces the water content in comparison with the reference measurement, which explains the negative values.

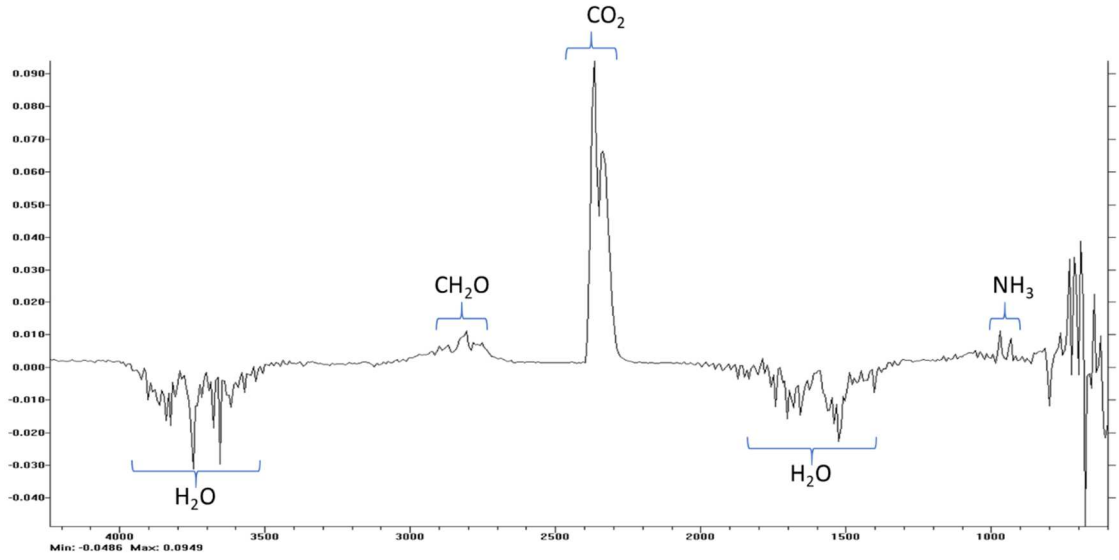



Figure 3. The infrared spectrum of wood waste degradation products by steam cooking

## 3.2. Confirmation of using FTIR as a replacement to HPLC for measurement of ammonia and formaldehyde

Formaldehyde, which is transferred from the wood waste to the gas (as is liquidated in the condenser), is generally measured by HPLC (Ihnát et al., 2017; Lee et al., 2014). However, since HPLC measurement requires a long time for each sample, using FTIR directly for analyzing outlet steam was tested. The test was performed at 3.5 bar, 10g/min steam flow, and 40g initial dried crushed wood waste. Every 6 minutes, liquid samples are recovered for the HPLC test, while FTIR measures formaldehyde and ammonia on-line. The result is shown in Fig. 4.

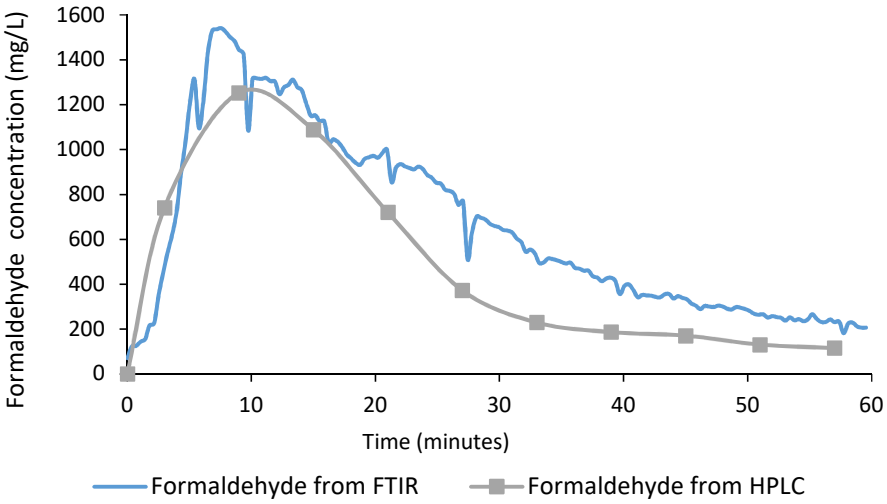



Figure 4. Comparing the concentration of formaldehyde during the steam cooking test measured by HPLC and FTIR

As shown in Figure 4, the results obtained from HPLC and FTIR are reasonably close to each other. Therefore, for the rest of the tests, FTIR is used to measure the outlet steam directly.

## 3.3 Effect of Steam ratio on steam cooking of wood waste

The first studied parameter was the steam ratio. Fig. 5 (a) and (b) show the results of formaldehyde and ammonia removal. As it can be seen from the curves below, whether for formaldehyde or ammonia, the flow of pollutants eliminated during the tests increases rapidly before decreasing throughout the test. The elimination of formaldehyde is almost complete at the end of the test in one hour, while this is not the case for ammonia.

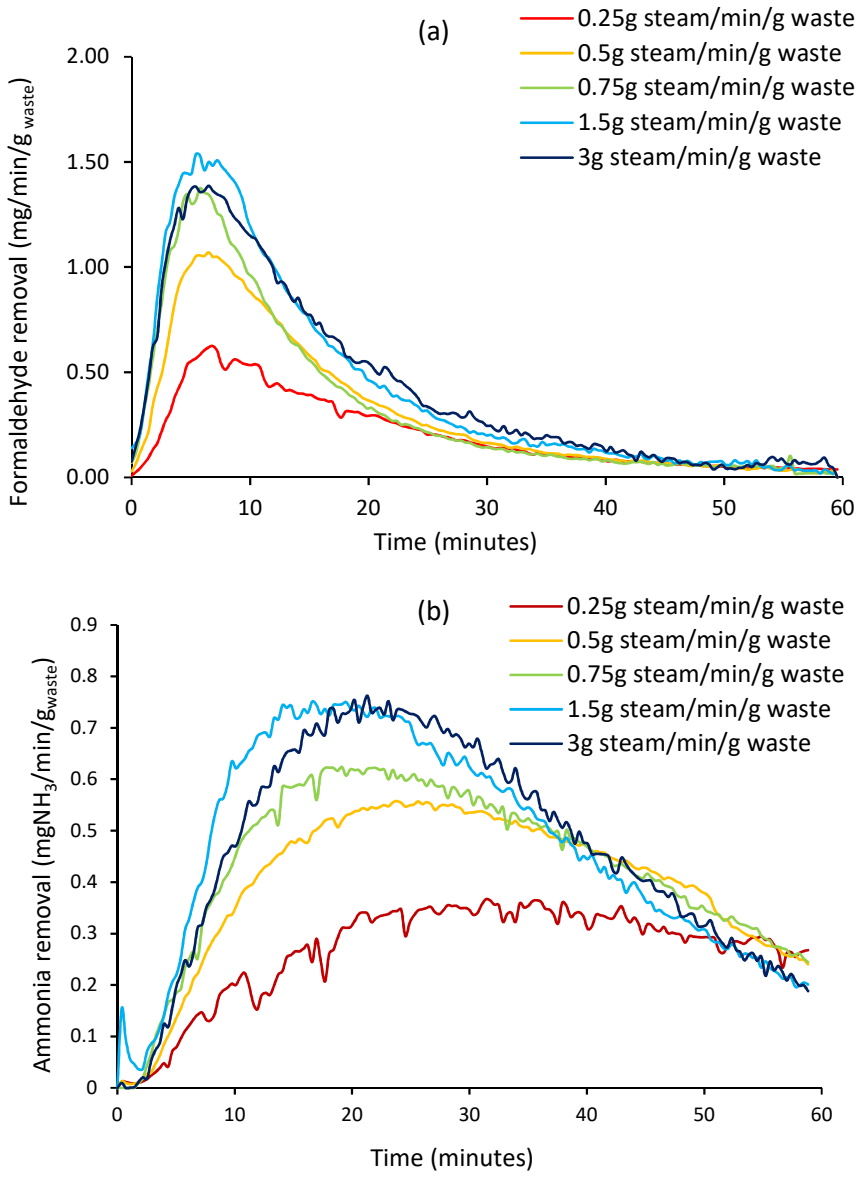



Figure 5. (a) Formaldehyde and (b) ammonia emissions as a function of time and steam/wood waste ratio.

Integrating these curves makes it possible to determine the total amount of formaldehyde and ammonia removed during the test. The results can be seen in Fig. 6.

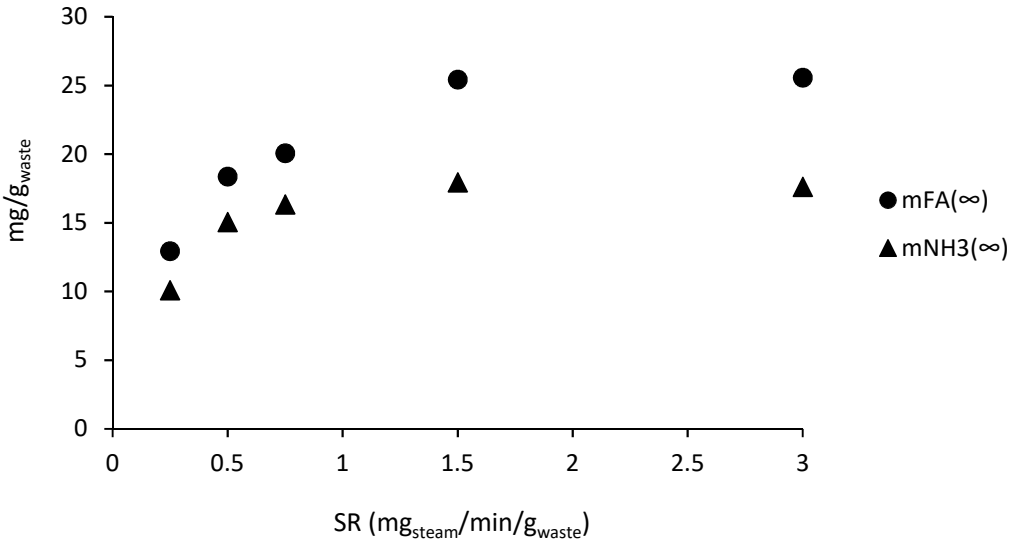



Figure 6. Effect of steam ratio (SR) on the total removal of formaldehyde and ammonia.

It can be seen that by increasing the flow per gram of initial mass, the total mass of both ammonia and formaldehyde increases until a certain point (over 1.5 steam ratio values). The quantity of formaldehyde released is in the range of 13 to 25.5 mg per gram of waste while the one of ammonia is between 10.1 to 17.6 $mg_{NH3}/g_{waste}$. Comparing these results with the literature is difficult since, to our knowledge, no article reports results concerning ammonia and formaldehyde released in the gas phase. All references dealing with the hydrolysis of UF resin (Myers and Koutsky, 1990; Ringena et al., 2006; Park and Jeong, 2011; Park and Causin, 2013; Lubis and Park, 2018; Grigsby et al., 2014), wood waste such as Particleboard (Lykidis and Grigoriou, 2008; Wan et al., 2014), and MDF (Wan et al., 2014; Hagel and Saake, 2020; Lubis et al., 2018; Lubis et al., 2020; Kraft and Roffael, 2003; Grisgby et al., 2014) present analyzes of the hydrolysate in the liquid phase. Some studies carried out in the liquid phase were at atmospheric pressure and not under pressurized steam (Lykidis and Grigoriou, 2008; Wan et al., 2014; Hagel and Saake, 2020).

Nevertheless, not all data from different studies can be compared. Concerning ammonia, it is reported that the formation of free ammonia from the degradation of cured UF resins leads to the formation of ammonium ions ($NH_4OH^-$) in the solution and an increase in the pH of the extract solution (Lubis and Park, 2018; Lubis et al., 2021). Only the pH of the solution is therefore measured as an indicator of ammonia production, but it remains a qualitative analysis. Moreover, a competition between acid release by wood hydrolysis (acetic and formic acid) in severe conditions and ammonia production makes it impossible to use only pH to quantify ammonia production (Hagel and Saake, 2020).

Another possible way to quantify ammonia is nitrogen titration in the liquid phase. Some authors (Lubis and park, 2018; Lubis et al., 2020; Kraft and Roffael, 2003; Grisgby et al., 2014) report such measurements, but the calculation of ammonia production is never have been done. Only nitrogen balance is performed to evaluate the reliability of the results.

Concerning formaldehyde release, different studies (Ringena et al., 2006; Park and Lee, 2015; Lubis and Park, 2018; Lubis et al., 2020) report formaldehyde titration in the liquid phase, but tests were performed on UF resin and not on waste wood. Values reported vary between 1 to 70 mg/g of resin; still, it remains difficult to compare. Lykidis and Grigoriou, 2008 and Wan et al., 2014, who worked on wood waste steam hydrolysis, only measured the free formaldehyde emissions at the surface of panel boards produced with the hydrolysed waste wood. Only Kraft and Roffael, (2003), who studied

the hydrolysis of MDF samples in water at a temperature between 100°C and 130°C (pressure not defined) for 20 minutes, reported formaldehyde release between 21.6 to 34.2 mg/g of waste which is quite similar to results provided in the presented study.

To evaluate the accuracy of FTIR measurement, a comparison between the nitrogen removal rate (wt. %) calculated from online gas analysis and from solid analysis (nitrogen content before and after steam cooking measured by Kjeldahl analysis) is performed. which the result is shown in Fig. 6. Even if values are quite similar (except for the 0.25 steam ratio), it is noticeable that the trends given by FTIR analysis (an increase of the nitrogen removal with steam ratio) are no more discernable with results obtained through Kjeldahl analysis. This point could be explained by the fact the loss of mass during the test has not been taken into account in the calculation of the nitrogen removal through Kjeldahl analysis. Fig. 7 shows that the sum of the mass of formaldehyde and ammonia removed during the test per gram of sample is between 23 to 43 mg which corresponds to 2.3 to 4.3% of mass loss. The characterization of hydrolysis production in part 3.1 also reveals the presence, in low quantities, of carbon dioxide which conducts to a higher loss of mass. Taking into account this increasing mass loss with steam ratio, it can be assumed that the nitrogen removed calculated from the solid analysis will therefore follow the same trends like the one obtained with FTIR measurements.

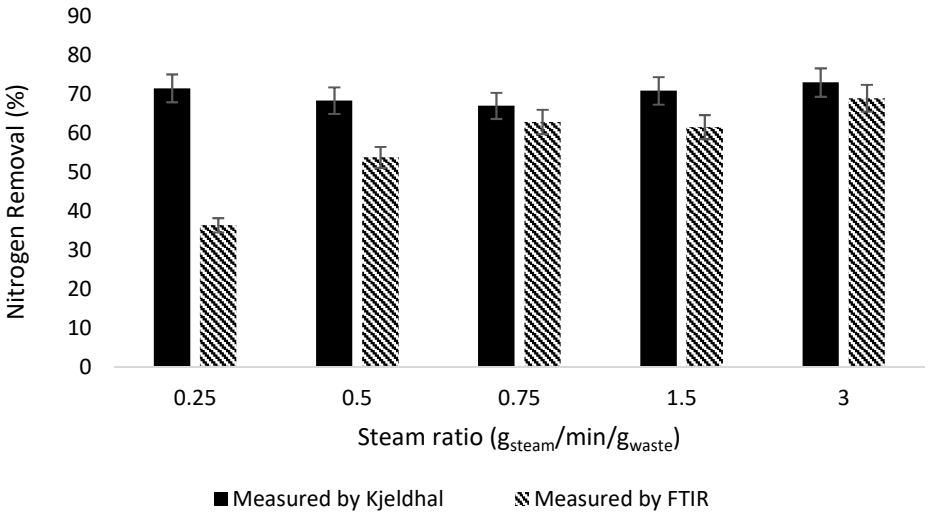
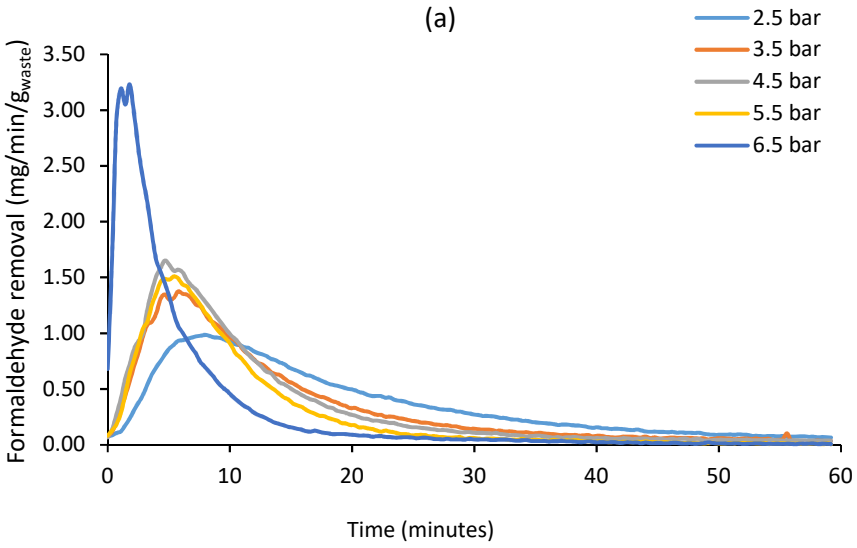



Figure 7. Comparison of nitrogen removal using the Kjeldahl method and FTIR analysis according to steam ratio.

The percentage of nitrogen eliminated is between 36.4 and 69%, according to the results obtained by gas analysis, while it is about 70% according to the analysis of solids. Considering the loss of mass of the samples, the values obtained by analysis of the solids would tend to increase. This indicates that the nitrogen removal rate is either overestimated by the solid analysis or underestimated by the gas analysis. It is quite difficult to conclude the origin of these discrepancies. Nevertheless, these values are consistent and in agreement with Lubis et al. (2018) who reported a nitrogen removal in the range of 40 to 80% for 2 hours for a MDF sample hydrolysis test in water between 40°C and 100°C.

## 3.4 Effect of pressure/temperature on steam cooking of wood waste

The next studied parameter was the pressure/temperature couple. The results can be seen in Fig. 8 (a) and (b). It is clear from these curves that pressure/temperature has a positive effect on the rate of pollutant removal in the same way.



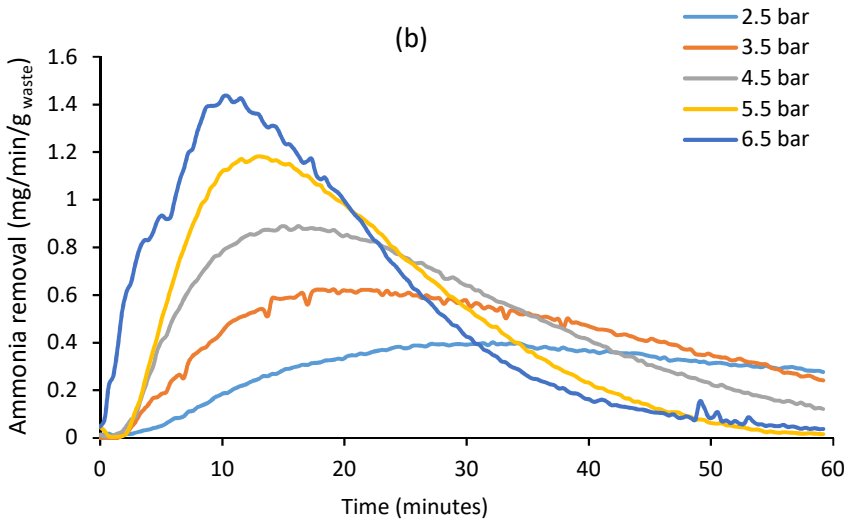




Figure 8. Effect of pressure/temperature on (a) formaldehyde and (b) ammonia removal from wood waste.

As previously explained, the total quantity of formaldehyde and ammonia eliminated during each test is determined by integrating the curves. The results are shown in Fig. 9.

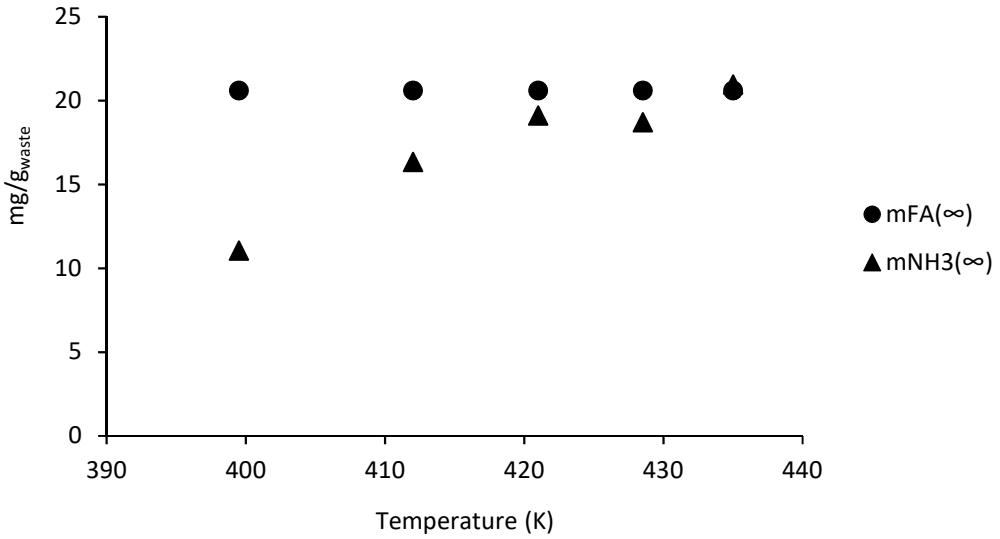



Figure 9. Effect of temperature on the total removal of formaldehyde and ammonia.

From the results obtained above, it can be interpreted that whatever the conditions were, formaldehyde elimination was almost complete after one hour of the experiment. The total mass of formaldehyde is independent of the temperature and reaches 20.6 mg of formaldehyde per gram of waste.

Regarding ammonia, elimination is almost complete for the two highest pressures (5.5 and 6.5 bars), while it is not complete for the lower pressures. The mass of ammonia eliminated increases with pressure. However, it is difficult at this stage to say whether this is an effect of the pressure/temperature or whether it is only because the reaction does not have enough time to complete over the entire duration of the test. The released quantities of ammonia are between 11 to 21 $mg_{NH3}$ /$g_{waste}$.

Fig. 10 shows the evaluation of the reliability of FTIR measurements. The conclusions are entirely similar to the conclusions made in the previous paragraph. The trend of increasing nitrogen removal rate with the severity of treatment with gas analysis (from 33.2 to 58.1%) is much less in comparison to the results obtained by solids analysis (67 to 72%). This is due to the fact that mass loss was not taken into account during the tests. Similarly, a significant difference is observed between the values obtained by solids analysis, which are overestimated compared to gas analysis. The results are consistent and comparable to those obtained by Lubis et al. (2018).

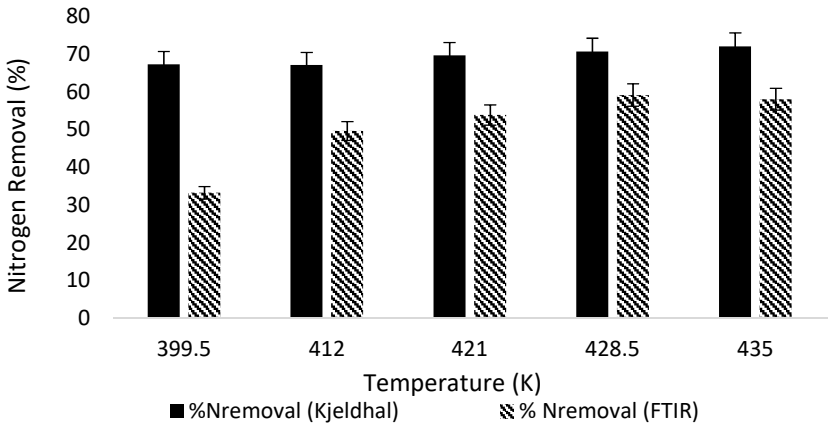



Figure 10. Comparison of nitrogen removal using the Kjeldahl method and FTIR analysis according to temperature.

## 3.4 Modelling ammonia and formaldehyde removal from wood waste

### 3.4.1 Description of the model

It is tried here to find a model which describes as best as possible emissions of both formaldehyde and ammonia from wood waste through hydrolysis according to experiments operatory conditions. The modeling will not concern the tests for a steam ratio of 1.5 and 3 as the masses of the samples are not 40g.

Initially, it was considered that the wood waste consists of wood and UF resin. Therefore:
wood waste = $\lambda_W \times$ wood + $\lambda_R \times$ Resin (1)

$\lambda_W$ and $\lambda_R$ are the relative mass contents of wood and resin respectively in $^{g_{wood}}/_{g_{wood\ waste}}$ and $^{g_{resin}}/_{g_{wood\ waste}}$.

The model consists of numerically evaluating the production rates ($g_{compound}/min/g_{waste}$) and the cumulative masses ($g_{compound}/g_{waste}$) of formaldehyde and ammonia emitted during the hydrolysis reaction. These species are emitted during the degradation of the UF resin and not of the wood, so the model is focused only on the degradation of the resin and not that of the sample as a whole.

According to the literature (Myers, 1986), the crosslinking of UF resins takes place according to several (reversible) dehydration reactions, which take place simultaneously in series and in parallel to form increasingly high molecular weight urea and formaldehyde polymers. Examples of these reversible reactions, for lower molecular weights, are given here:

$OC(NH_2)_2 + HOCH_2OH \rightleftharpoons H_2NCONHCH_2OH + H_2O$ (2)
urea (U) formaldehyde (F) monomethylolurea (UF)

$H_2NCONHCH_2OH + HOCH_2OH \rightleftharpoons HOCH_2NHCONHCH_2OH + H_2O$ (3)
monomethylolurea (UF) formaldehyde (F) dimethylolurea (FUF)

$H_2NCONHCH_2OH + OC(NH_2)_2 \rightleftharpoons (H_2NCONH)_2CH_2 + H_2O$ (4)
monomethylolurea (UF) urea (U) methylenediurea (UFU)

$2\times H_2NCONHCH_2OH \rightleftharpoons (H_2NCONHCH_2)_2O + H_2O$ (5)
monomethylolurea (UF) dimethyleneurea ether (UFOFU)

A very simplified reaction mechanism is then proposed to describe the hydrolysis phenomenon of the resin present in the waste. The solid R (resin) is modified during a first hydrolysis reaction to give an intermediate compound I without producing formaldehyde or ammonia. The intermediate compound I then corresponds to the partially depolymerized resin. In turn, it degrades during reaction 2 into urea (U) and formaldehyde (FA). Urea is then finally degraded into gaseous ammonia ($NH_3$) and carbon dioxide ($CO_2$) during reaction 3. $\alpha$, $\beta_{NH3}$, $\beta_{FA}$, $\gamma$ and $\gamma_C$ correspond respectively to the masses of I (partially depolymerized resin), U, FA, $NH_3$, and $CO_2$ produced per unit mass of parent compounds. Thus, the units of $\alpha$, $\beta_{NH3}$, $\beta_{FA}$, $\gamma$ and $\gamma_C$ are respectively $^{g_I}/_{g_R}$, $^{g_U}/_{g_I}$, $^{g_{FA}}/_{g_I}$, $^{g_{NH_3}}/_{g_U}$, and $^{g_{CO_2}}/_{g_U}$. The reaction mechanism can thus be outlined as below:

$R \xrightarrow{+ H_20\ (k_1)} \alpha \times I$ (6)

$$I \xrightarrow{+H_20\ (k_2)} \beta_{NH3} \times U + \beta_{FA} \times FA \quad (7)$$

$$U \xrightarrow{+H_20\ (k_3)} \gamma \times NH_3 + \gamma_C \times CO_2 \quad (8)$$

Assuming that the kinetic laws of degradation are in first order with respect to the reactants and in zero-order with respect to the water vapor (present in large quantities and therefore content is stable during the reaction), the material balances of the compounds are as follows:

- Solids (resonated on the mass–closed system): $\left(\left(g_{compound}/\min\right)/g_{waste}\right)$

$$dm_R(t)/dt = -k_1 \times m_R(t) \quad (9)$$

$$dm_I(t)/dt = \alpha \times k_1 \times m_R(t) - k_2 \times m_I(t) \quad (10)$$

$$dm_U(t)/dt = \beta_{NH3} \times k_2 \times m_I(t) - k_3 \times m_U(t) \quad (11)$$

- Gas (resonated on the density – open system): $\left(\left(g_{compound}/\min\right)/g_{waste}\right)$

$Q \times \rho_i$ represents the flow rate of species leaving the reactor through the outlet pipe;

$V_g \times d\rho_i(t)/dt$ represents the variation of the mass of species within the reactor;

With $V_g$, the reactor volume (2.5 L) and Q, the steam flow in L/min (taking into account the temperature and pressure conditions within the reactor). The analytical integration of the differential equations is not essential, a so-called “iterative” numerical method is used here. Knowing the initial value of each of the masses (or densities) ($R(0) = \lambda_R$; $I(0) = U(0) = \rho_{NH3}(0) = \rho_{FA}(0) = 0$), the initial value of the variation rate of the mass (or density) of species can be determined ($dm_i(0)/dt$ or $d\rho_i(0)/dt$). Considering this value remains constant between two measurement steps (iteration step = 0.1 minutes), the value of the quantities at the next iteration step can then be determined by the following equation:

$m_{i(n+1)} = m_{i(n)} + dm_{i(n)}/dt \times \Delta t$, with $\Delta t$ the sampling time; $\Delta t = 0.1$ min

The production rates of formaldehyde and ammonia $\left(\left(g_{compound}/\min\right)/g_{waste}\right)$ emitted during the hydrolysis reaction as a function of time are represented by the term $Q \times \rho_i(t)$. The cumulative masses $\left(g_{compound}/g_{waste}\right)$ of formaldehyde and ammonia emitted per unit mass of sample during the hydrolysis reaction are determined according to the following equation:

$$m_i(t+\Delta t) = m_i(t) + Q \times \rho_i(t) \quad (15)$$

For each experimental condition, error functions (sum of the squared difference between the calculated and the experimental values) on the production rates $\left(erfc\ dm_{NH_3}\ and\ erfc\ dm_{FA}\right)$ are calculated. These different error functions can be added as needed to optimize the desired

parameters according to the different tests to be taken into account. All errors obtained are summarized in Table 2.

Table 2. Error function table

| | | | $NH_3$ | FA |
|---|---|---|---|---|
| **T°C** | **T(K)** | **SR** | **erfc $dm_{NH3}$** | **erfc $dm_{FA}$** |
| **148** | 412 | 0.25 | 1.85 | 1.58 |
| **148** | 412 | 0.5 | 0.93 | 1.30 |
| **148** | 412 | 0.75 | 0.10 | 2.39 |
| **Sum "Effect SR"** | | | 2.88 | 5.27 |
| **139** | 412 | 0.75 | 0.35 | 5.43 |
| **148** | 421 | 0.75 | 0.10 | 2.39 |
| **155.5** | 428.5 | 0.75 | 0.31 | 6.63 |
| **162** | 435 | 0.75 | 2.85 | 34.30 |
| **168** | 441 | 0.75 | 2.71 | 49.52 |
| **Sum "Effect T"** | | | 6.32 | 98.27 |
| **Sum "Effect SR and T"** | | | 9.20 | 103.54 |
| **Global sum of error functions** | | | 112.74 | |

## 3.4.2 Determination of the parameters of the model

### 3.4.2.1 Determination of parameters α and γ (constants)

α, represents the ratio between the mass of the intermediate compound I produced ($M_I$) and the mass of the compound R consumed ($M_R$):

$$\alpha = {M_I}/{M_R} \quad (16)$$

The first reaction of the proposed reaction mechanism (eq 6) is considered representative of the depolymerization of the resin (by hydrolysis) without the production of urea, formaldehyde, or ammonia. This reaction can then be similar to the breaking of methylene ether bridges by hydrolysis (inverse of the fourth reaction for the production of dimethylurea ether (eq 5)). These are present throughout the cross-linked network of the UF resin and do bind not only resin monomers (monomethylolurea) but also dimers, trimers as well as a wide variety of fragments of varying degrees of polymerization. The precise determination of the parameter α is therefore theoretically impossible. Nevertheless, by doing the calculation for the case of the fourth reaction (Eq. 5) written in the direction of hydrolysis this time, the following equation can be obtained:

$$H_2NCONH\text{-}CH_2OCH_2\text{-}HNOCNH_2 + H_2O \rightleftharpoons 2(H_2NCONHCH_20H) \quad (17)$$

dimethylurea ether (UFOFU) + water 2 × monomethylolurea (UF)

The first reaction of the proposed mechanism (eq 6) reacting one mole of compound R with one mole of water to give one mole of compound I, which can be explained as below:

$$M_I = M_R + M_{H_20} \quad (18)$$

Thus, by combining equations (16) and (18):

$$\alpha = \left(M_R + M_{H_20}\right) / M_R \quad (19)$$

Considering that R represents the UFOFU dimer and based on equation (19), the following equation can be obtained:

$$\alpha = \left(M_{UFOFU} + M_{H_20}\right) / M_{UFOFU} = (162+18) / 162 = 1.11 \quad (20)$$

In this specific case, the value of α is 1.11. For the other cases, which necessarily involve fragments of larger molecular weights, the value of α will decrease and tend towards 1 for the highest molar masses. Thus, even if the value of α cannot be calculated precisely, it is between 1 and 1.11. Therefore, it was set to 1 for convenience. The reaction is then considered as depolymerization without gaining mass, at least not significant given the high molecular weight of the resin fragments. The value of α is not decisive for the model.

Regarding γ, it is worth considering the last reaction of the proposed mechanism (eq 8), which describes the hydrolysis of urea into ammonia and carbon dioxide:

$$\underset{(60\ g)}{OC(NH_2)_2} + \underset{(18\ g)}{H_20} \leftrightharpoons \underset{(34\ g)}{2\ NH_3} + \underset{(44\ g)}{CO_2} \quad (21)$$

For 1g of urea consumed, 0.567g of ammonia (34/60) is produced. Therefore, the value of γ is set to 0.567.

#### 3.4.2.2 Determination of other model parameters:

Determination of the parameters value and the kinetic constants was carried out according to different methods based on different hypotheses:

- Case 1: The rate constants $k_i$ only depends on the temperature;
  - Case 1-a: $\beta_{NH3}$ and $\beta_{FA}$ are variable; $\lambda_R$, α, and γ are constants
  - Case 2-a: $\lambda_R$ is variable; $\beta_{NH3}$ and $\beta_{FA}$ are constants
- Case 2: The rate constants $k_i$ depends on the temperature and steam ratio. Other parameters remain constant.

##### 3.4.2.2.1 Case 1-a:

The rate constants $k_1$, $k_2$, and $k_3$ only depend on the temperature according to the Arrhenius law:

$$k_i(T) = k_{0i} \times \exp\left(-Ea_i / R.T\right) \quad (22)$$

In order to account for the effect of the vapor ratio (SR) on the final quantities of formaldehyde and ammonia emitted, the values of specific parameters are dependent on SR.

- $\lambda_R$: $\lambda_R$ is the theoretical mass content of resin. Based on particleboard and MDF content in waste wood, the UF glue content as the resin is around 10%. Knowing that in the batch of wood waste used in this study, the rate of particleboard and fiberboard is around 80%, the UF resin content in the samples is then around 8%. The value of $\lambda_R$ is then fixed at 0.08 $g_{resin} / g_{wood\ waste}$ knowing that this value is not decisive.
- $\beta_{NH3}$ and $\beta_{FA}$: these parameters are independent of temperature but dependent on the value of the steam ratio. Therefore, it was decided to use the cumulative masses of formaldehyde and ammonia experimentally measured during the experimental tests. According to the

numerical model proposed, for 1 g of wood waste, the theoretical masses $\left({}^{g_{compound}}/_{g_{waste}}\right)$ at infinity mass of formaldehyde $m_{FA}(\infty)$ and of ammonia $m_A(\infty)$ are equal to:

$$m_{FA}(\infty)= \lambda_R \times \alpha \times \beta_{FA} \quad (23)$$

$$m_{NH_3}(\infty)= \lambda_R \times \alpha \times \gamma \times \beta_{NH_3} \quad (24)$$

It appears here that the values of $\lambda_R$ and $\alpha$ are not decisive as the parameters $\beta_{NH3}$ and $\beta_{FA}$ will be determined from the experimental values of the theoretical masses when hydrolysis is completed and from the product $\lambda_R \times \alpha$. Thus, if the value of this product is changed, the values of $\beta_{NH3}$ and $\beta_{FA}$ will be changed proportionally without changing anything in the model. Since this cannot be determined experimentally, it is impossible to verify whether the value of the various parameters is correct. It is only the value of the product of these different parameters that influence the result in terms of the amount of ammonia and formaldehyde produced. For formaldehyde, the values of $m_{FA(\infty)}$ according to the different parameters are known as the reaction is complete after of experiment period regardless of the conditions. The values of $\beta_{FA}$ can then be deduced from the experimental values according to the expression:

$$\beta_{FA\_exp}\ (T, SR)= {}^{m_{FA}(\infty)(T, SR)}\Big/_{(\lambda_R \times \alpha)} \quad (25)$$

An evolution in logarithmic form makes it possible to adequately describe the evolution of $\beta_{FA}$ as a function of steam ratio using the following equation:

$$\beta_{FA\_Calc} = 0.1082 \times \ln(SR) + 0.2886 \quad (26)$$

The values of $\beta_{FA\_Exp}$ and $\beta_{FA\_Calc}$ are presented in Table 3.

Table 3. Values of $\beta_{FA\_Exp}$, $\beta_{FA\_Calc}$, $\beta_{NH_3\_Opt}$ and $\beta_{NH_3\_Calc}$

| SR | T (°C) | T (K) | $m_{FA}(\infty)$ | $\beta_{FA\_exp}$ | $\beta_{FA\_calc}$ | $m_{NH3}(\infty)$ | $\beta_{NH3\_opt}$ | $\beta_{NH3\_calc}$ |
|---|---|---|---|---|---|---|---|---|
| 0,25 | 148 | 421 | 0,01295 | 0,1619 | 0,1387 | 0,0101 | 0,2225 | 0,2830 |
| 0,5 | 148 | 421 | 0,01837 | 0,2296 | 0,2136 | 0,0151 | 0,3322 | 0,3961 |
| 0,75 | 148 | 421 | 0,0206 | 0,2575 | 0,2575 | 0,0164 | 0,4621 | 0,4623 |
| 0,75 | 139 | 412 | 0,0206 | 0,2575 | 0,2575 | 0,0111 | 0,4621 | 0,4623 |
| 0,75 | 148 | 421 | 0,0206 | 0,2575 | 0,2575 | 0,0164 | 0,4621 | 0,4623 |
| 0,75 | 155.5 | 428.5 | 0,0206 | 0,2575 | 0,2575 | 0,0191 | 0,4621 | 0,4623 |
| 0,75 | 162 | 435 | 0,0206 | 0,2575 | 0,2575 | 0,0187 | 0,4621 | 0,4623 |
| 0,75 | 168 | 441 | 0,0206 | 0,2575 | 0,2575 | 0,0210 | 0,4621 | 0,4623 |

For ammonia, the values of $mNH_3(\infty)$ as a function of the various parameters are unknown as the reaction is not complete at the end of the experiment period except for the test at 435K for a steam ratio of 0.75. For this condition, the value of $\beta_{NH3\_Exp}$ (0.75) can then be deduced from the experimental value according to the following expression:

$$\beta_{NH_3\_Exp}\ (0,75)= {}^{m_{NH_3}(\infty)(435\ ;0,75)}\Big/_{(\lambda_R \times \alpha \times \gamma)} = {}^{0,0209}\Big/_{(0,08 \times 1 \times 0,567)} = 0,462 \quad (27)$$

The values of $\beta_{NH3}$ for the other values of steam ratio will then be obtained by optimization. Knowing the values of the different parameters of $\lambda_R$, $\alpha$, and $\beta_{FA}$, the optimization of the kinetic parameters $k_{01}$, $E_{a1}$, $k_{02}$, and $E_{a2}$ is carried out by minimizing the sum of the error functions obtained for formaldehyde on the production rate ($\mathrm{erfc}\ dm_{FA}$) for conditions where the temperature is variable

(yellow box on table 2). Knowing only the value $\beta_{NH_3\_Exp}$ (0.75) = 0.462 for a steam ratio of 0.75, the values of the kinetic parameters $k_{03}$ and $E_{a3}$ are optimized only for the tests with a steam ratio of 0.75 and with temperatures variables by minimizing the sum of the error functions obtained for ammonia on the production rate ($erfc_{dm\_NH3}$, the orange box on table 2). The values of the $\beta_{NH3}$ for the different values of steam ratio are optimized one by one. Knowing the evolution of the values of $\beta_{NH3\_Opt}$ as a function of steam ratio, an equation is used to calculate these values as a function of steam ratio according to the following expression:

$$\beta_{NH_3\_Calc} = A \times \ln(SR) + B \quad (28)$$

The constants A and B as well as the kinetic parameters $k_{03}$ and $E_{a3}$ are finally optimized simultaneously for all the tests (green box on table 2).

$$\beta_{NH_3\_Calc} = 0.1632 \times \ln(SR) + 0.5093 \quad (29)$$

The values of $\beta_{NH3\_Opt}$ and $\beta_{NH3\_Calc}$ are listed in Table 3.

The velocity laws are assumed to be of zero-order concerning the water vapor, assumed to be in large quantities. As a result, the values of k determined previously are "apparent" values and the "real" k depends on the density of the water vapor pressure under the conditions of the various tests:

$$k_{apparent} = k_{real} \times \rho_{water} \quad (30)$$

Based on the ideal gas law, the density of water according to the experimental conditions (Pressure and Temperature) is calculated with the following equation:

$$\rho_{water}(P, T) = \frac{P \times M_{water}}{RT} \quad (31)$$

The value of $k_{i\_apparent}$ is then divided by the density of the saturation vapor pressure $\rho_{water}$ for the conditions of the various tests. The $k_{i\_real}$ of the three reactions is plotted as $\ln(k_{i\_real}) = f(1/T)$ to determine the new values of $k_{0i\_real}$ and $E_{ai\_real}$.

3.4.2.2.2 Case 1-b:

As it was shown that the evolution trends of $\beta_{NH3}$ and $\beta_{FA}$ values follow a similar shape, it is expected that evolution trends for $\lambda_R$ could also be represented by a logarithmic form according to the eq (32):

$$\lambda_R = C \times \ln(SR) + D \quad (32)$$

$\lambda_R$ is then no longer considered as the resin content in the waste but as the reactive part of the resin, which depends only on the value of the steam ratio. The kinetic constants $k_{0i\_real}$ and $E_{ai\_real}$ remain unchanged as do the values of α and γ. The values used for $\beta_{NH3}$ and $\beta_{FA}$, those obtained for an steam ratio of 0.75 are $\beta_{NH_3}$=0,462 $\beta_{FA}$=0,2575. The values of C and D are optimized by minimizing the global sum of the error functions on the production rate (grey boxes in table 2):

$$\lambda_R = 0.0313 \times \ln(SR) + 0.0887 \quad (33)$$

3.4.2.2.3 Case 2:

The values of $\lambda_R$, α, and γ remain unchanged from case 1-a ($\lambda_R$ =0.08; α=1; γ=0.567). The values used for $\beta_{NH3}$ and $\beta_{FA}$ are those obtained for a steam ratio of 0.75 ($\beta_{NH3}$= 0.462, $\beta_{FA}$ = 0.2575). The rate

constant $k_{1\_real}$ follows Arrhenius law; It is therefore only dependent on the temperature and not on the steam ratio:

$$k_{1\_real}(T)=k_{01\_real}\times \exp\left(^{-Ea_{1\_real}}/_{R.T}\right) \quad (34)$$

The rate constants $k_2$ and $k_3$ are both dependent on T (according to Arrhenius law) and steam ratio:

$$k_{i\_real}(T)=k_{0i\_real}\times \exp\left(^{-Ea_{i\_real}}/_{R.T}\right)\times\exp\left(^{-H_i}/_{SR}\right) \quad (35)$$

The dependence of the constants $k_2$ and $k_3$ with respect to the value of the steam ratio is explained by taking into account transfer phenomena at the surface of the sample. By increasing the ratio of water vapor to the mass of the sample (SR), the concentration of water vapor at the surface of the sample increases which leads to an increase in the rate of the reaction.

The values of the parameters $\lambda_R$, $\alpha$, and $\beta_{FA}$ being known, the kinetic parameters $k_{01}$, $E_{a1}$, $k_{02}$ and $E_{a2}$ (dependence of $k_1$ and $k_2$ as a function of T) and the parameter relating to the dependence of $k_2$ with the value of steam ratio (H2) are optimized by minimizing the sum of the errors obtained for formaldehyde on the production rate (box in yellow in Table 2). The value of $\beta_{FA}$ is then optimized and obtained as $\beta_{FA}$ =0.237.

The values of the parameters $\lambda_R$, $\alpha$, $\gamma$, and $\beta_{NH3}$ are known. The kinetic parameters $k_{03}$ and $E_{a3}$ (dependence of $k_3$ as a function of T) and the parameter relating to the dependence of $k_3$ with the value of the steam ratio (H3) are optimized by minimizing the sum of the errors obtained for ammonia both on the cumulative mass and on the production rate (box in orange in the table of errors). The value of $\beta_{NH3}$ is then optimized and obtained as $\beta_{NH3}$ =0.476.

### 3.4.3 Presentation and comparison of model results:

All the model parameters for the different cases studied are listed in Tables 4 and 5. The three approaches considered for the model made it possible to represent the production of formaldehyde and ammonia as a function of time and the cumulative masses eliminated during the tests for all assessed conditions. Here only the curves relating to Case 1-b are shown to avoid confusion (Fig. 11 to 14).

Table 4. Kinetic parameters of the model for the 3 cases studied

| | | **Case 1-a** | | **Case 1-b** | | **Case 2** | |
|---|---|---|---|---|---|---|---|
| | | $K_{01}$ | $E_{a1}$ or $H_1$ | $K_{01}$ | $E_{a1}$ or $H_1$ | $K_{01}$ | $E_{a1}$ or $H_1$ |
| **Temperature effect** | Stage 1 | 3.36E+06 | 5.74E+04 | 3.36E+06 | 5.74E+04 | 1.25E+06 | 5.40E+04 |
| | Stage 2 | 1.74E-01 | 4.35E+03 | 1.74E-01 | 4.35E+03 | 2.13E-01 | 2.44E+03 |
| | Stage 3 | 2.77E+00 | 1.69E+04 | 2.77E+00 | 1.69E+04 | 6.29E+00 | 1.98E+04 |
| **Steam ratio effect** | Stage 2 | - | | - | | - | 4.31E-01 |
| | Stage 3 | | | | | | 9.44E-02 |

Table 5. Stoichiometric parameters of the model for the three cases studied

| | **Case 1-a** | **Case1-b** | **Case 2** |
|---|---|---|---|
| $\boldsymbol{\lambda_R}$ | 0,08 | 0,0313×LN(SR) + 0,0887 | 0,08 |
| $\boldsymbol{\alpha}$ | 1 | 1 | 1 |
| $\boldsymbol{\gamma}$ | 0,567 | 0,567 | 0,567 |

| | | | |
|---|---|---|---|
| $\beta_{FA}$ | 0,0882×LN(SR) + 0,2829 | 0,258 | 0,237 |
| $\beta_{NH3}$ | 0,1632×LN(SR) + 0,5093 | 0,462 | 0,476 |

610

611 The comparison of the different modeling approaches can be made by comparing the values of the
612 sums of the error functions given in Table 6. The values of the overall errors on the production rates
613 for the three cases are very similar (between 112 and 113). On the other hand, the difference is more
614 marked when comparing the overall errors on the cumulative masses this time (between 5431 and
615 7263). It seems the least efficient is Case 2, although it is the one that, from a physical point of view,
616 is closest to reality. Nevertheless, each approach makes it possible to obtain satisfactory
617 representations.

618

619

620

621

622

623

624

625

626

627

628

Table 6. The comparison of the different modeling approaches done by comparing the values of the sums of the error functions.

| | | | erfc production flow | | | | | | erfc cumulated masses | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Case 1-a | | Case 1-b | | Case 2 | | Case 1-a | | Case 1-b | | Case 2 | |
| | | | $NH_3$ | FA | $NH_3$ | FA | $NH_3$ | FA | $NH_3$ | FA | $NH_3$ | FA | $NH_3$ | FA |
| T°C | T(K) | SR | erfc $dm_{NH3}$ | erfc $dm_{FA}$ | erfc $dm_{NH3}$ | erfc $dm_{FA}$ | erfc $dm_{NH3}$ | erfc $dm_{FA}$ | erfc $m_{NH3}$ | erfc $m_{FA}$ | erfc $m_{NH3}$ | erfc $m_{FA}$ | erfc $m_{NH3}$ | erfc $m_{FA}$ |
| 148 | 421 | 0.25 | 1.09 | 1.58 | 1.11 | 1.86 | 0.32 | 4.66 | 275.23 | 221.27 | 123.01 | 166.82 | 74.91 | 2463.83 |
| 148 | 421 | 0.5 | 0.55 | 1.30 | 0.68 | 1.18 | 0.07 | 0.99 | 137.99 | 310.08 | 256.14 | 187.66 | 8.07 | 160.91 |
| 148 | 421 | 0.75 | 0.06 | 2.39 | 0.06 | 2.40 | 0.08 | 0.86 | 2.94 | 392.44 | 5.73 | 373.93 | 10.18 | 66.33 |
| Sum "Effect SR" | | | 1.70 | 5.27 | 1.85 | 5.43 | 0.46 | 6.50 | 416.16 | 923.79 | 384.88 | 728.40 | 93.17 | 2691.07 |
| 139 | 412 | 0.75 | 0.21 | 5.43 | 0.20 | 5.46 | 0.10 | 2.64 | 25.99 | 1343.23 | 27.61 | 1374.95 | 23.32 | 1482.13 |
| 148 | 421 | 0.75 | 0.06 | 2.39 | 0.06 | 2.40 | 0.08 | 0.86 | 2.94 | 392.44 | 5.73 | 373.93 | 10.18 | 66.33 |
| 155.5 | 428.5 | 0.75 | 0.18 | 6.63 | 0.20 | 6.59 | 0.28 | 10.20 | 68.59 | 474.37 | 91.83 | 445.41 | 60.97 | 285.50 |
| 162 | 435 | 0.75 | 1.69 | 34.30 | 1.69 | 34.20 | 2.13 | 44.06 | 142.24 | 664.09 | 115.86 | 640.77 | 257.52 | 1039.01 |
| 168 | 441 | 0.75 | 1.60 | 49.52 | 1.64 | 49.55 | 1.87 | 41.11 | 91.82 | 698.40 | 121.19 | 684.67 | 37.82 | 883.04 |
| Sum"Effect T" | | | 3.74 | 98.27 | 3.78 | 98.20 | 4.46 | 98.86 | 331.58 | 3572.52 | 362.23 | 3519.72 | 389.83 | 3756.01 |
| Sum (Effect SR and T) | | | 5.44 | 103.54 | 5.63 | 103.63 | 4.93 | 105.36 | 747.73 | 4496.30 | 747.10 | 4248.12 | 483.00 | 6447.08 |
| Global sum of error functions | | | 108.98 | | 109.26 | | 110.29 | | 5244.04 | | 4995.23 | | 6930.08 | |

629

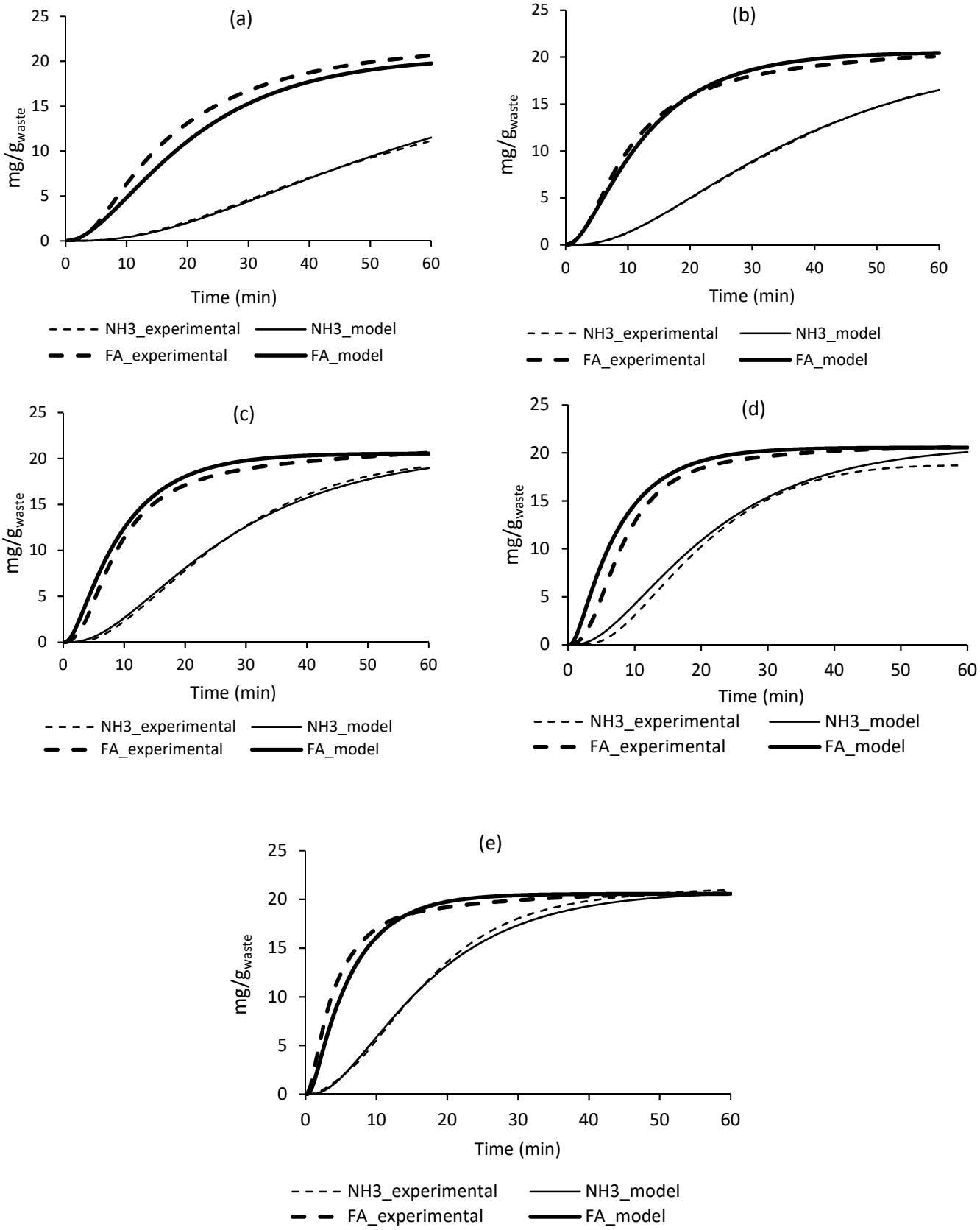



Figure 11. Effect of steam ratio on cumulative masses of FA and $NH_3$ emitted from wood waste under (a) 2.5 bar, (b) 3.5 bar, (c) 4.5 bar, (d) 5.5 bar, and (e) 6.5 bar.

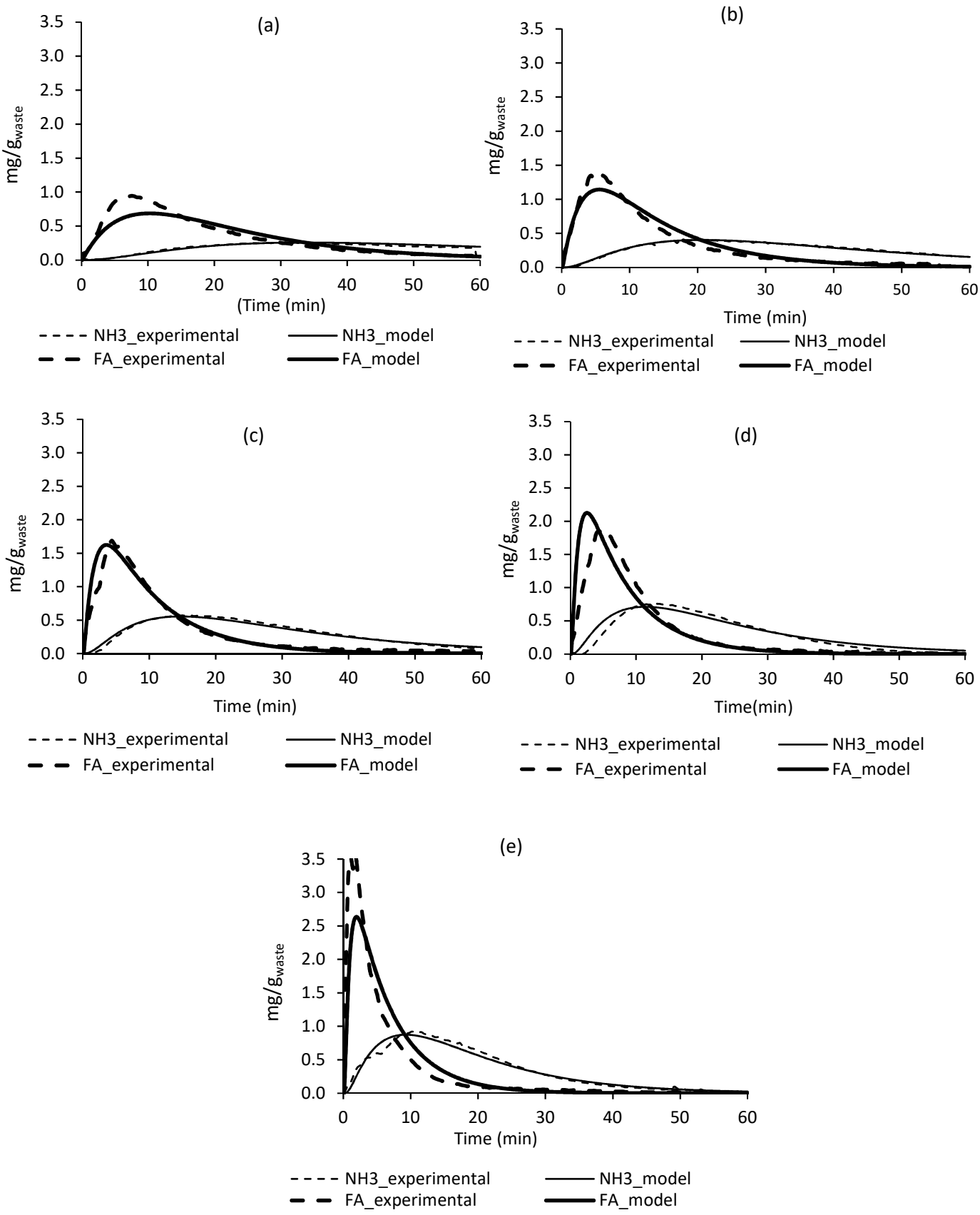
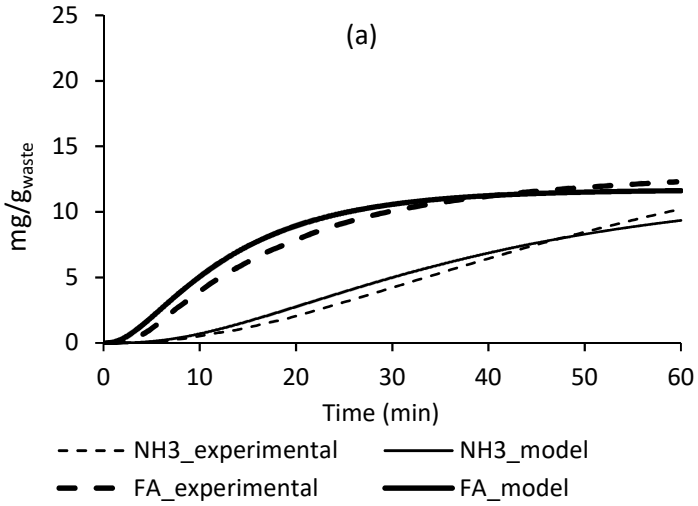
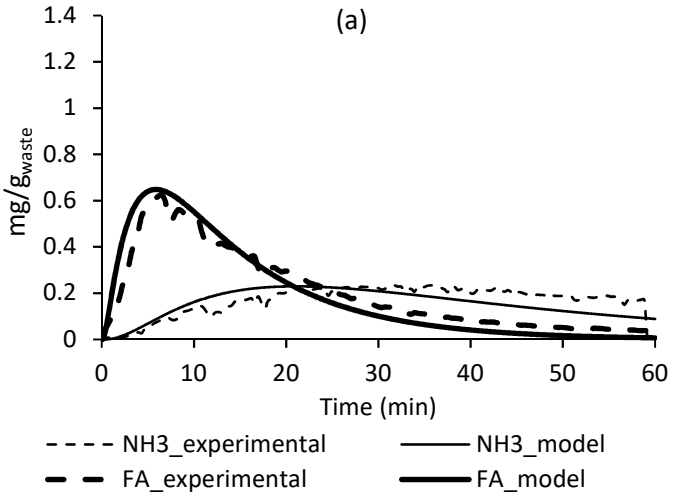
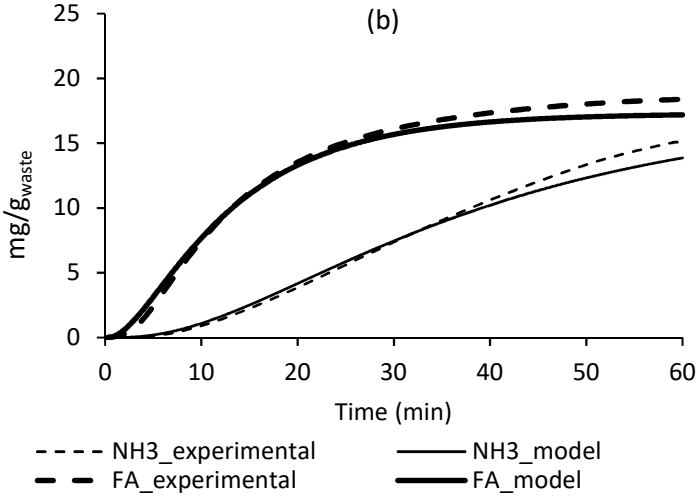
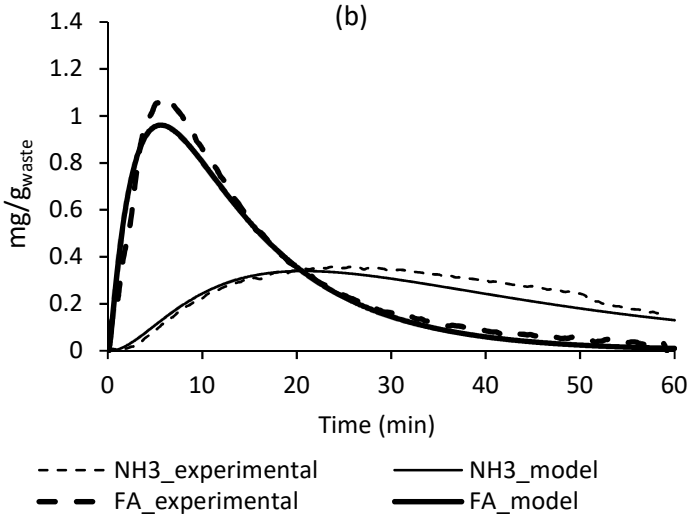


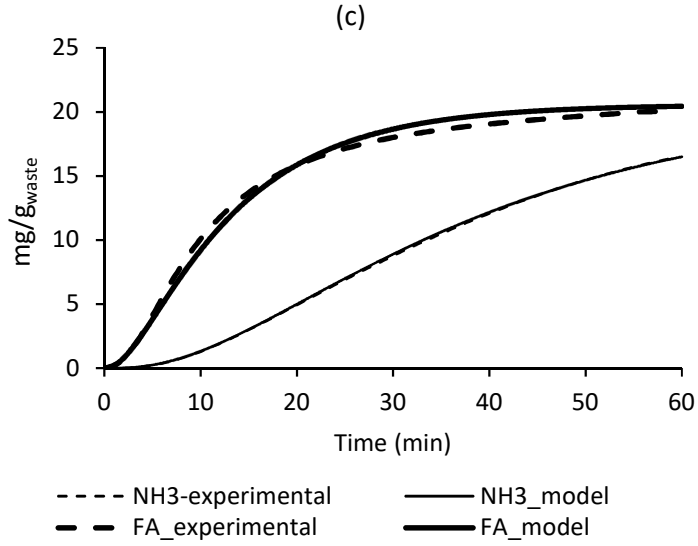

Figure 12. Effect of temperature on outlet flow of FA and $NH_3$ emission from wood waste under (a) 2.5 bar, (b) 3.5 bar, (c) 4.5 bar, (d) 5.5 bar, and (e) 6.5 bar.



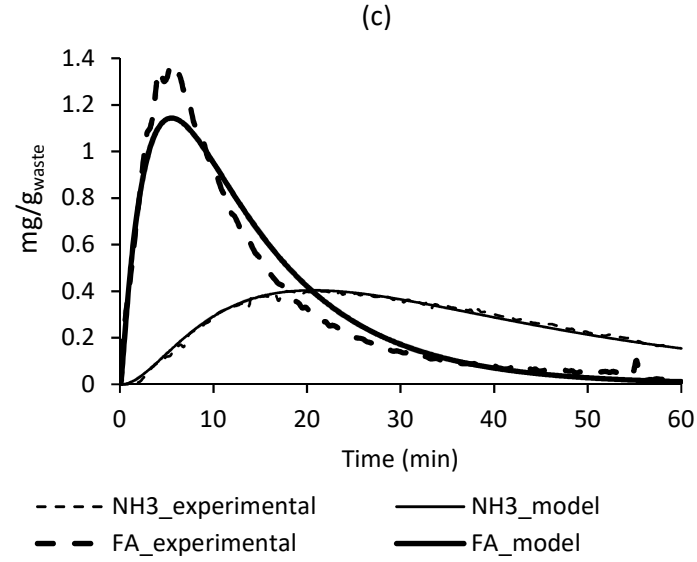




Figure 13. Effect of steam ratio on cumulative masses of FA and $NH_3$ emitted from wood waste at steam ratio of (a) 0.25, (b) 0.5, and (c) 0.75 under 3.5 bar.

Figure 14. Effect of steam ratio on outlet flow of FA and $NH_3$ emission from wood waste at steam ratio of (a) 0.25, (b) 0.5, and (c) 0.75 under 3.5 bar.

# 4. Conclusion

The effect of pressure/temperature and the steam ratio on the hydrolysis of wood waste has been investigated. It could be first noticed that an original method to analyze gas emissions under rich water vapor atmosphere by FTIR measurement has successfully been used.

The hydrolysis gas products were mainly formaldehyde and ammonia, while carbon dioxide was also produced in low quantities. The evaluation of the effect of the steam ratio shows a dependence of the quantity of formaldehyde and ammonia released below 1.5 $g_{steam}/min/g_{waste}$. A plateau is observed for higher steam ratio values.

The evaluation of the effect of the pressure/temperature couple shows that total formaldehyde emissions are independent of this factor. This point has not been experimentally demonstrated, but the numerical model based on this assumption allows to well represent the experimental evolution of ammonia.

The nitrogen removal rate in the range of 33 to 70% is reached, which shows the efficiency of the hydrolysis process to remove resin from waste. Nitrogen balance shows a good correlation between nitrogen elimination calculated from gas and solid analysis highlighting the reliability of the FTIR measurement method, which also is confirmed by formaldehyde analysis using HPLC in the liquid phase.

Finally, the three approaches proposed in this work for the numerical modelisation of ammonia and formaldehyde emissions according to operatory conditions give all a good fitting between experimental and calculated values. All information regarding quantification of ammonia and formaldehyde emissions as well as numerical modelization could now be used as reliable technical results to study the scale-up of such a process.

**Authors Contributions:** All authors have read and agree to the published version of the manuscript. **Maximilien GIBIER:** Conceptualization, methodology, writing—original draft preparation **Mohammad SADEGHISADEGHABAD:** Experimental work, formal analysis, writing—original draft preparation **Pierre GIRODS:** methodology, formal analysis, numerical modelization, writing—original draft preparation, writing—review and editing **André ZOULALIAN:** numerical modelization **Yann ROGAUME**: Supervision, Funding acquisition

**Funding:** This research was funded by the Grand-Est region.

**Acknowledgments:** Authors wish to thank VALDELIA French Company for supplying the waste material used in this work.

**Conflicts of interest:** The authors declare no conflicts of interest.

# 5. Reference


Bernstein, A., Sargent, E. H., Aspuru-Guzik, A., Cogdell, R., Fleming, G. R., Van Grondelle, R., & Molina, M. (2016). Renewables need a grand-challenge strategy. *Nature*, *538*(7623), 30-30. https://doi.org/10.1038/538030a

Besserer, A., Troilo, S., Girods, P., Rogaume, Y., & Brosse, N. (2021). Cascading recycling of wood waste: A review. *Polymers*, *13*(11), 1752. https://doi.org/10.3390/polym13111752

Cowling, E. B., & Merrill, W. (1966). Nitrogen in wood and its role in wood deterioration. Canadian Journal of Botany, 44(11), 1539-1554. https://doi.org/10.1139/b66-167

Waste furniture sector France. (2020). Annual report of the Waste furniture sector in France. https://librairie.ademe.fr/dechets-economie-circulaire/1714-rapport-annuel-de-la-filiere-des-dechets-d-elements-d-ameublement-dea-donnees-2018.html

Girods, P. (2008). *Procédé multi-étagé de valorisation de déchets bois type panneaux de particules* (Doctoral dissertation, Université Henri Poincaré-Nancy 1).

Girods, P., Dufour, A., Rogaume, Y., Rogaume, C., & Zoulalian, A. (2008). Thermal removal of nitrogen species from wood waste containing urea formaldehyde and melamine formaldehyde resins. *Journal of Hazardous Materials*, *159*(2-3), 210-221. https://doi.org/10.1016/j.jhazmat.2008.02.003

Girods, P., Dufour, A., Rogaume, Y., Rogaume, C., & Zoulalian, A. (2009a). Comparison of gasification and pyrolysis of thermal pre-treated wood board waste. *Journal of Analytical and Applied Pyrolysis*, *85*(1-2), 171-183. https://doi.org/10.1016/j.jaap.2008.11.014

Girods, P., Dufour, A., Fierro, V., Rogaume, Y., Rogaume, C., Zoulalian, A., & Celzard, A. (2009b). Activated carbons prepared from wood particleboard wastes: Characterisation and phenol adsorption capacities. *Journal of Hazardous Materials*, *166*(1), 491-501. https://doi.org/10.1016/j.jhazmat.2008.11.047

Grigsby, W. J., Thumm, A., Carpenter, J. E., & Hati, N. (2014). Investigating the extent of urea formaldehyde resin cure in medium density fibreboard: Characterisation of extractable resin components. *International Journal of Adhesion and Adhesives*, *50*, 50-56. https://doi.org/10.1016/j.ijadhadh.2013.12.020

Hagel, S., & Saake, B. (2020). Fractionation of waste MDF by steam refining. *Molecules*, *25*(9), 2165. https://doi.org/10.3390/molecules25092165

Hepburn, J. S. (1908). The modifications of the Kjeldahl method for the quantitative determination of nitrogen. *Journal of the Franklin Institute*, *166*(2), 81-99. https://doi.org/10.1016/S0016-0032(08)90028-4

Ihnát, V., Lübke, H., Russ, A., & Borůvka, V. (2017). Waste agglomerated wood materials as a secondary raw material for chipboards and fibreboards Part I. Preparation and characterization of wood chips in terms of their reuse. *Wood research*, *62*(1), 45-56.

Irle, M., Barbu, M., Thoeman, H., Inggris, G. B., Irle, M., & Sernek, M. (2010). Wood based panels: an introduction for specialists. *Wood-based Panel Technology,* Cost Action E49, 1.

Jiang, X., Li, C., Chi, Y., & Yan, J. (2010). TG-FTIR study on urea-formaldehyde resin residue during pyrolysis and combustion. *Journal of Hazardous Materials*, *173*(1-3), 205-210. https://doi.org/10.1016/j.jhazmat.2009.08.070

Kraft, R., & Roffael, E. (2003). Thermohydrolytischer abbau von mitteldichten faserplatten. *adhäsion KLEBEN & DICHTEN*, *47*(10), 38-41. https://doi.org/10.1007/BF03244013

Lee, M., Prewitt, L., & Mun, S. P. (2014). Formaldehyde release from medium density fiberboard in simulated landfills for recycling. *Journal of the Korean Wood Science and Technology*, *42*(5), 597-604. https://doi.org/10.5658/WOOD.2014.42.5.597

Li, J., Zhu, J., & Ye, L. (2007). Determination of formaldehyde in squid by high-performance liquid chromatography. *Asia Pac. J. Clin. Nutr*, *16*(1), 127-130.

L Liu, M., Wang, Y., Wu, Y., & Wan, H. (2018). Hydrolysis and recycling of urea formaldehyde resin residues. *Journal of Hazardous Materials*, *355*, 96-103.. https://doi.org/10.1016/j.jhazmat.2018.05.019

Lubis, M. A. R., Hong, M. K., & Park, B. D. (2018). Hydrolytic removal of cured urea–formaldehyde resins in medium-density fiberboard for recycling. *Journal of Wood Chemistry and Technology*, *38*(1), 1-14. https://doi.org/10.1080/02773813.2017.1316741

Lubis, M. A. R., & Park, B. D. (2018). Analysis of the hydrolysates from cured and uncured urea-formaldehyde (UF) resins with two F/U mole ratios. *Holzforschung*, *72*(9), 759-768. https://doi.org/10.1515/hf-2018-0010.

Lubis, M. A. R., Hidayat, W., Zaini, L. H., & Park, B. D. (2020). Effects of Hydrolysis on the Removal of Cured Urea-Formaldehyde Adhesive in Waste Medium-Density Fiberboard. *Jurnal Sylva Lestari*, *8*(1), 1-9. https://doi.org/10.23960/jsl181-9

Lubis, M. A. R., Manohar, S. Y., Laksana, R. P. B., Fatriasari, W., Ismayati, M., Falah, F., ... & Hidayat, W. (2021). The Removal of Cured Urea-Formaldehyde Adhesive Towards Sustainable Medium Density Fiberboard Production: A Review. *Jurnal Sylva Lestari*, *9*(1), 23-44. https://doi.org/10.23960/jsl1923-44.

Lubke, H., Ihnát, V., Kuňa, V., & Balberčák, J. (2020). A multi-stage cascade use of wood composite boards. *Wood Res*, *65*, 843-854.

Lykidis, C., & Grigoriou, A. (2008). Hydrothermal recycling of waste and performance of the recycled wooden particleboards. *Waste Management*, *28*(1), 57-63. https://doi.org/10.1016/j.wasman.2006.11.016

Myers, G.E., (1986). Mechanisms of Formaldehyde Release from Bonded Wood Products, in: Formaldehyde Release from Wood Products, ACS Symposium Series. American Chemical Society, pp. 87–106. https://doi.org/10.1021/bk-1986-0316.ch008.

Myers, G.E., (1982). Hydrolytic stability of cured urea-formaldehyde resins. *Journal of Wood Science*, 2, 127–138

Myers, G. E., & Koutsky, J. A. (1990). Formaldehyde Liberation and Cure Behavior of Urea-Formaldehyde Resins. *Holzforschung*, *44*(2), 117-126. https://doi.org/10.1515/hfsg.1990.44.2.117

Nishikawa, H., & Sakai, T. (1995). Derivatization and chromatographic determination of aldehydes in gaseous and air samples. *Journal of Chromatography A*, *710*(1), 159-165. https://doi.org/10.1016/0021-9673(94)01006-Z

Park, B. D., & Causin, V. (2013). Crystallinity and domain size of cured urea–formaldehyde resin adhesives with different formaldehyde/urea mole ratios. *European Polymer Journal*, *49*(2), 532-537. https://doi.org/10.1016/j.eurpolymj.2012.10.029

Park, B. D., & Jeong, H. W. (2011). Hydrolytic stability and crystallinity of cured urea–formaldehyde resin adhesives with different formaldehyde/urea mole ratios.

*International Journal of Adhesion and Adhesives*, *31*(6), 524-529. https://doi.org/10.1016/j.ijadhadh.2011.05.001

Park, B. D., & Lee, S. M. (2015). Hydrolytic Stability of Cured Urea-Melamine-Formaldehyde Resins Depending on Hydrolysis Conditions and Hardener Types. *Journal of the Korean Wood Science and Technology*, *43*(5), 672-681. https://doi.org/10.5658/WOOD.2015.43.5.672

Pizzi, A. and Mittal, K. L., eds. (2003). *Handbook of Adhesive Technology* , 2nd edn, New York, NY: Marcel Dekker. https://doi.org/10.1201/9780203912225

Ren, T., Wang, Y., Wu, N., Qing, Y., Li, X., Wu, Y., & Liu, M. (2022). Degradation of urea-formaldehyde resin residues by a hydrothermal oxidation method into recyclable small molecular organics. *Journal of Hazardous Materials*, *426*, 127783. https://doi.org/10.1016/j.jhazmat.2021.127783

Ringena, O., Janzon, R., Pfizenmayer, G., Schulte, M., & Lehnen, R. (2006). Estimating the hydrolytic durability of cured wood adhesives by measuring formaldehyde liberation and structural stability. *Holz als Roh-und werkstoff*, *64*(4), 321-326. https://doi.org/10.1007/s00107-005-0087-3

Samaržija-Jovanović, S., Jovanović, V., Konstantinović, S., Marković, G., & Marinović-Cincović, M. (2011). Thermal behavior of modified urea–formaldehyde resins. *Journal of thermal analysis and calorimetry*, *104*(3), 1159-1166. https://doi.org/10.1007/s10973-010-1143-8

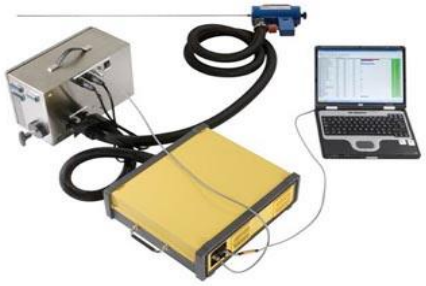
Wahed, P., Razzaq, M. A., Dharmapuri, S., & Corrales, M. (2016). Determination of formaldehyde in food and feed by an in-house validated HPLC method. *Food chemistry*, *202*, 476-483. https://doi.org/10.1016/j.foodchem.2016.01.136

Wan, H., Wang, X. M., & Shen, J. (2014). Recycling wood composite panels: Characterizing recycled materials. *BioResources*, *9*(4), 7554-7565.

Xu, X., Su, R., Zhao, X., Liu, Z., Li, D., Li, X., ... & Wang, Z. (2011). Determination of formaldehyde in beverages using microwave-assisted derivatization and ionic liquid-based dispersive liquid–liquid microextraction followed by high-performance liquid chromatography. *Talanta*, *85*(5), 2632-2638. https://doi.org/10.1016/j.talanta.2011.08.037

Inlet wood waste

Steam generator

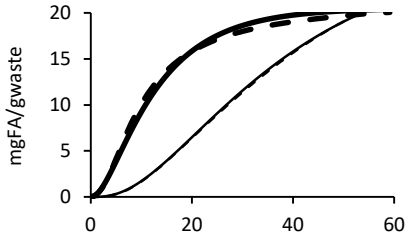



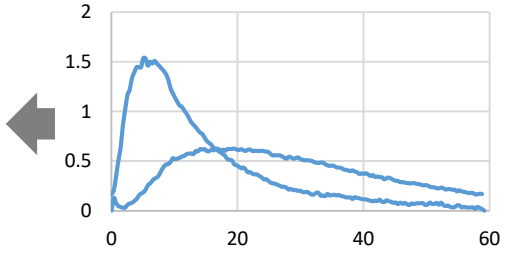
FTIR on line measurements of ammonia and formaldehyde emissions

Hydrolysis Reactor

Outlet depolluted wood waste

Mathematical modeling




Operatory conditions:

- Pressure/Temperature
- Duration
- Steam flow