

A PILOT STUDY FOR THE PYROLYSIS OF THE UREA FORMALDEHYDE-MELAMINE FORMALDEHYDE RESIN PAPER WASTE

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Producing pyrolytic oil via pyrolysis reaction from waste papers containing melamine formaldehyde and urea formaldehyde, which have an economic and environmental value, is the base of this study. In this study gas, liquid and solid products were gained via pyrolysis, and liquid products are put into perspective from the point of energy. In this pilot study, positive results were obtained for comprehensive further experiments, and it's seen that the results may have meaningful value on sectoral basis with regards to reducing environmental damages of the wastes and energy producing.

Key Words: Pyrolysis, Urea Formaldehyde, Melamine Formaldehyde, Paper, Impregnation, Energy Production, Wastes.

1. Introduction

Energy consumption, efficiency and the effects of energy problems on the environment are the most important items on the agenda globally. Within this framework, assessment of a variety of waste for energy production forms one of the most important fields of study currently and in the recent past. One of the most important headings in the use of waste for energy production is evaluation of industrial waste as an energy resource. Disposal of industrial waste in its current form or removal from trash and use in recycling and energy production are alternatives that should be dealt with both for environmental awareness and economically.

In this study, the focus is on producing liquid fuel from urea formaldehyde (UF) and melamine formaldehyde (MF) resin paper waste, known in short industrially as impregnated paper waste, with the pyrolysis method.

The pyrolysis method is the most appropriate chemical process used to obtain fluid from biomass mainly from long-chain cellulosic structures. Biomass pyrolysis is commonly completed at temperatures between 300 to 700 °C. Different temperature stages produce products with different properties and compositions [1]. Pyrolysis provides solid, fluid and gas phase products from biomass and it is possible to obtain fuel from each phase with different pyrolysis applications [2].

The pyrolysis method is based on degradation of biomass with the effect of heat in an oxygen-free environment [3]. The pyrolysis application may be simply divided into 3 classes as slow, fast and flash [4]. These classifications are made linked to the speed of the temperature increase during the pyrolysis reaction. Traditional pyrolysis, known as slow pyrolysis, generally has low productivity, with fast and flash pyrolysis methods chosen for more productive applications.

Elements affecting the pyrolysis product combinations and yield may be listed as the reaction temperature, heating rate, retention time, inert gas flux, pressure, catalyst, pyrolysis atmosphere and particle size [5,6].

This study was prepared based on the idea that decor paper containing urea formaldehyde (UF) – melamine formaldehyde (MF) resin or waste resin paper from the preparatory stages for use in the wood industry could be assessed for energy production.

Paper containing UF and MF resin is used for decorative covering and to develop surface characteristics of material like wood-based planks, floor covering or door panels in the wood sector. As with any type of production, waste is created from these products due to non-standard quality values or production conditions.

Though waste comprising paper containing UF and MF may be re-evaluated for production, this situation forms a risk in terms of maintaining stability of production conditions.

The waste material dealt with in this study may be defined as a composite material of the combination of raw decorative paper and thermoset resin. Annually an estimated 1 ~ 1.2 million tons of raw decorative paper are produced, which is equivalent to production of roughly 2 ~ 2.5 tons UF/MF resin paper according to the sectoral information. If 1% is considered the most optimistic estimate of the amount of waste, a stable idea about the dimensions of the topic globally may be obtained.

In the literature, though there are studies on the separate pyrolysis of paper and UF and MF resins, or description of UF – MF resin wood panel pyrolysis, there is no study of pyrolysis of UF-MF resin paper encountered. For identification of whether pyrolysis of paper and UF-MF resins together is possible or has applicable value in terms of fluid fuel production especially, this study was completed to obtain basic results before detailed studies about the topic are performed and to determine the necessary road map for advanced studies.

This study has the characteristics of a preliminary study about fuel production from pyrolysis of UF-MF resin paper and thus making this waste less harmful to the environment. The results are encouraging for more comprehensive studies to be performed on the topic, presenting significant infrastructure for the use of waste for researchers. Additionally, this study gains a new objective within the context of the pyrolysis method, commonly used for energy production from waste in the field of chemistry.

2. Similar Pyrolysis Procedures

In the literature, though there are no studies about pyrolysis of impregnated waste paper, there are studies about pyrolysis of similar wood panel waste containing resin and resin-free cellulosic material. Additionally, pyrolysis of MF and UF resins are among the studied topics. The general schematic of inputs and outputs for the pyrolysis procedure are given in Figure 1.

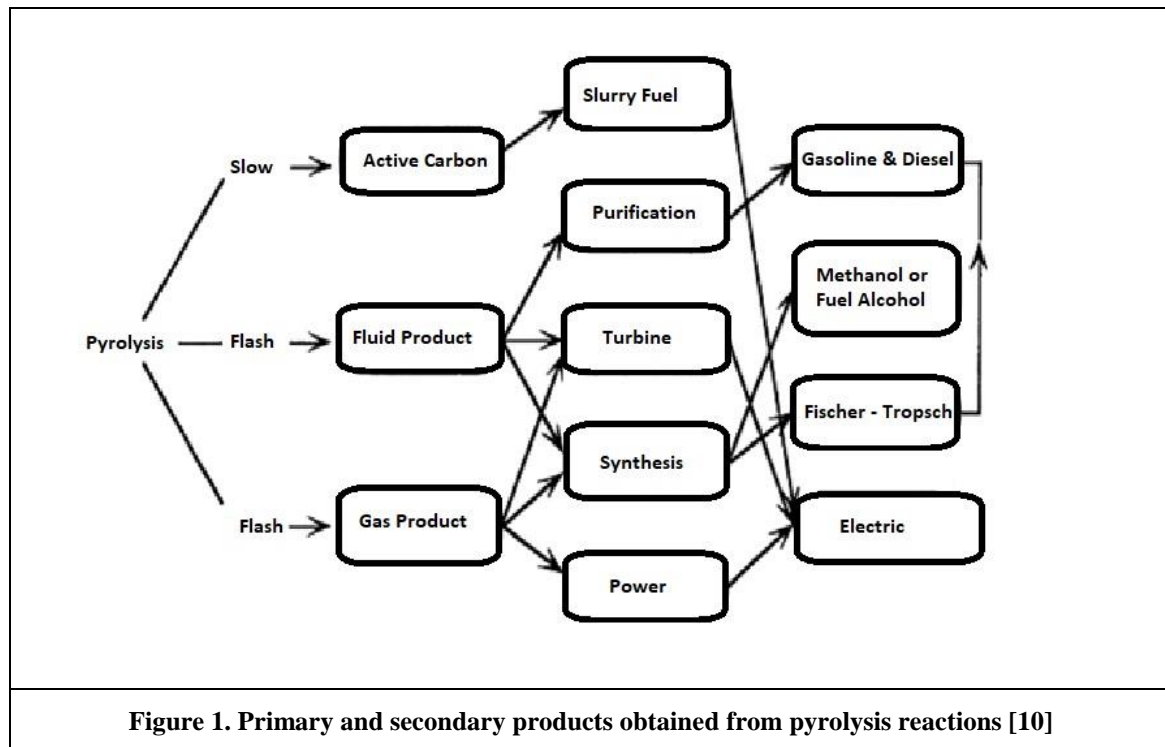
A study of pyrolysis of wood waste containing UF and MF observed that heat degradation of wood and heat degradation of the resin content occurred in different temperature intervals. When cellulosic pyrolysis conditions are investigated, the heat degradation of paper was understood to occur at different temperatures from UF and MF [2, 7]. Additionally, pyrolysis of cellulose with microwave radiation appeared to obtain successful results at about 200 °C temperature [8].

Another study of pyrolysis of non-impregnated UF with cellulose identified that UF had a slowing effect on the thermo-chemical degradation of cellulose [9]. This situation may be interpreted as due to the expansion in the difference between degradation temperatures of MF and cellulose, which are generally close.

Pyrolysis of material obtained by permeating paper with MF and UF resins in the impregnation process is expected to have different results from the total pyrolysis results of each separate component of the material. This is because there is a chance of interaction between each component in pyrolysis including the polymerization process of UF and MF paper. Generally, the heat degradation order in pyrolysis may be said to be UF, MF and cellulose.

The main problem with pyrolysis of UF and MF resins or material containing these polymers is the nitrogen content outputs and gas products at CO and CO₂ levels.

There are studies [7, 11, 12] about reducing the products involving nitrogen-based pollutants and chemicals containing cyanide or gasification of pre-processed waste to dispose of or reduce these types of



pollutant during the pyrolysis process applied at low temperatures to wood-based waste containing UF and MF. It is discussed whether pyrolysis is a more environmental choice than gasification or not [13].

When the studies mentioned above are investigated, it appears that pyrolysis of paper waste containing UF and MF is theoretically possible; however, a detailed investigation should be performed in terms of pollutants contained within pyrolysis products and the effects of pollutants should be considered in optimization studies for product combinations and energy efficiency.

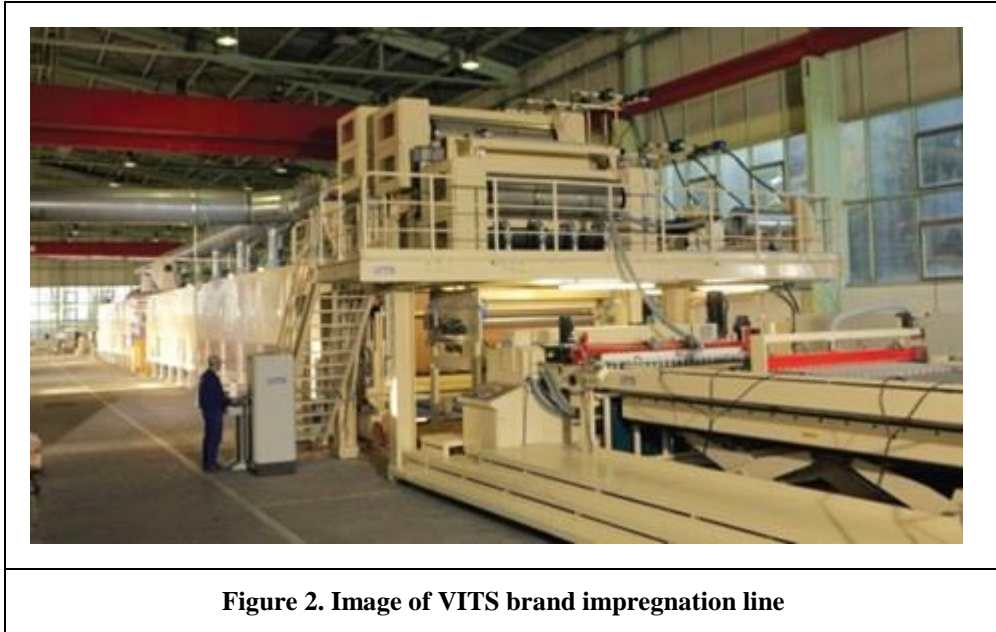
3. Impregnation Process and Resin Paper

The paper forming the topic of the study is paper waste impregnated with resin used to cover a variety of wood-based panels in the wood industry.

Wood-based panels are commonly used as raw material in the furniture sector. Wood-based panels are produced by pressing varying proportions of wood chips (small wood fragments) together with urea formaldehyde resin. To provide decorative properties to these panels, a method called melamine coating is applied.

Melamine coating is applied by gluing decor paper impregnated with urea formaldehyde and melamine formaldehyde resins with relatively smaller amounts of helpful chemicals (catalysts, wetting agent, mold-release agent, dust preventer, anti-blocking agent, varnish, etc.) to the upper and lower surfaces of wood-based panels in melamine presses.

Resin decor paper is cellulosic paper material processed with urea formaldehyde (UF) and melamine formaldehyde (MF) resins. To ensure the panels produced with the melamine coating process have the desired quality characteristics, the input properties of impregnated decorative papers (urea formaldehyde (UF) – melamine formaldehyde (MF) resin amounts, mixture ratios, reaction durations, molar rates, amount of additional chemicals used, etc.) and final properties (weight of impregnated paper, humidity of impregnated paper, etc.) should have certain values. This is in addition to sensitively setting mechanical and physical properties such as speed of the impregnation line, network tension of the line, temperatures of drying ovens used along the impregnation line, and speed, direction and form of preliminary wetting processes applied to the decor paper. The general appearance of this type of impregnation line is given in Figure 2.



In short, there are two stages to the passage of decor paper through the impregnation process: in the first stage, the paper is filled with UF resin and in the second stage the surface of the paper is covered with MF-dominated resin. Expanding as a result of these processes, an amount is cut off both sides of the paper and these sections are collected as waste. Additionally, impregnated paper waste is formed due to non-standard production and problems experienced during production.

The impregnated decor paper comprises nearly half resin and half paper. The aim of this study is to perform preliminary studies about pyrolysis of this waste and assessment as fuel. The appearance of impregnated paper waste used in the study is given in Figure 3.



4. Pyrolysis Experimental Setup

Ensuring the necessary conditions for the pyrolysis reaction is linked to the properties and appropriateness of reactor and devices. Control of factors like necessary temperature, pressure and retention time cannot be considered independent of the properties of the chosen equipment.

The basic aim of experiments was firstly to identify whether the required products could be obtained or not. Then the aim was to measure limited numbers of properties such as the mass distribution of product composition and fluid product.

The priority conditions necessary to provide the pyrolysis experimental setup for the experiments may be listed as ensuring an oxygen-free reaction environment, no leaks, ensuring inert gas flux, ensuring necessary retention duration, heating to desired temperature, ensuring fixed temperature, cooling products and collection of the fluid products.

The reactor dimensions and properties were identified by considering the reaction kinetics as much as possible. The reaction kinetics are represented by activation energy, reaction rate, order, reactant and product concentrations and reaction stages. 14.]

There is a variety of research in the literature about maximizing fluid product amounts based on pyrolysis conditions for biomass. In a variety of studies, particle sizes were chosen from 2-5 mm in general for heat transfer rate [15]. Reactor dimensions may be optimized according to different particle sizes [16].

Reaching the required activation energy for reaction of the material used is linked to ensuring necessary heat conduction within the reactor appropriately. In the study, the polymerization and pyrolysis stages for raw material with heterogeneous structure were followed. Transferring the necessary heat to the raw material in the reactions is not independent of the reactor's properties. The most important factor for heat transfer is water amount. Just as the water content of the raw material affects the reaction kinetics, it also affects heat transfer. A water content of 10% or lower is stated in the literature [17] as an element to reduce the amount of water content within the product and ensure appropriate heat transfer.

The reactor dimensions used in the study were determined as a result of experimental studies, instead of calculations, at a scale to ensure 30 g raw material with 5% humidity rates prepared with preliminary processes could enter a reaction under appropriate conditions.

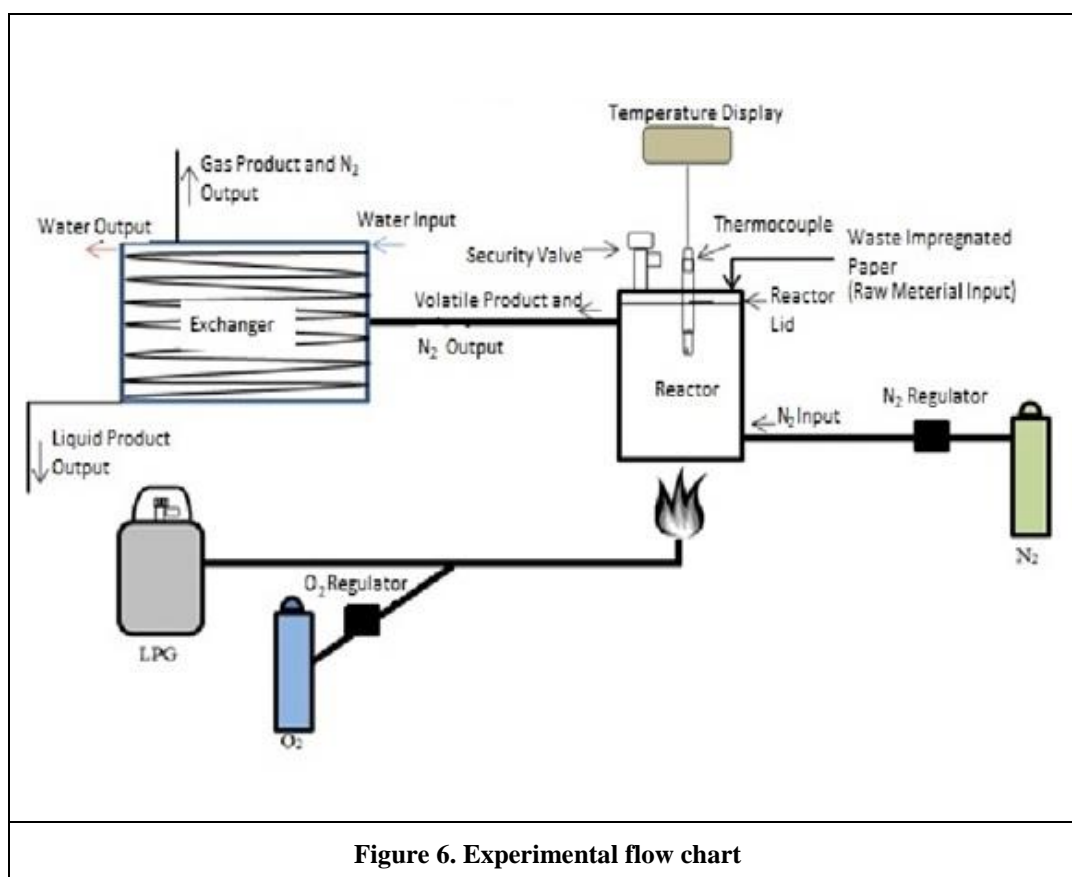
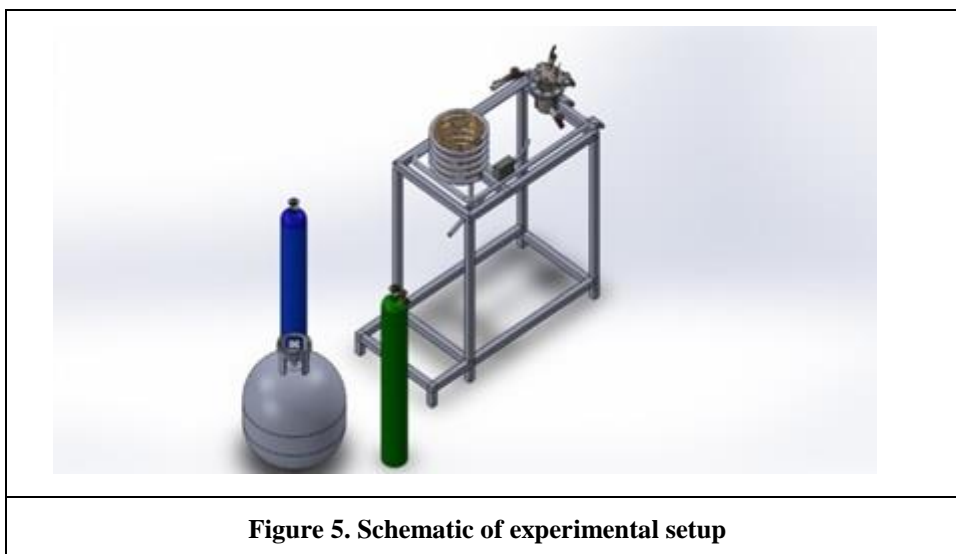
Pyrolysis is an endothermic process and requires sensitive setting of heat energy to bring the reactant into the reaction under the necessary conditions. In the literature [18], the total energy necessary for pyrolysis is linked to the raw material used and was identified as 1.0–1.8 mJ/kg.

The reactor used in the study was chosen with height of 15 cm and diameter of 10 cm. It was constructed of stainless steel. The general lines of the experimental system comprised nitrogen cylinder, reactor, exchanger, oxygen and liquid gas cylinders and torch for heating. The experimental setup can be seen in Figure 4.



Figure 4. General appearance of experimental setup

The general appearance of the experimental setup and reactor are given in Figure 5. Additionally, the operation of the experimental setup is detailed in the flow chart in Figure 6.



The reactor is heated by liquefied petroleum gas tube linked to a torch for heating. Though this heating method does not ensure very high heating rates, this setup provides a practical way to feed with raw material after high temperatures are reached and to observe the effect of high temperatures on the pyrolysis reaction and products.

Reactions occurred in three ways:

1. Heating to target temperature by feed with raw material with a certain initial temperature
2. Loading raw material after reaching target temperature
3. Applying retention times under both conditions.

The second application was used to see the results of rapid pyrolysis under available heating rate conditions.

The reactor used in the system contained one input for nitrogen and one output for product. With eight bolts, the reactor lid also has a pressure valve added for safety in situations with high temperature and pressure. A thermocouple and its digital readout measures the momentary temperature within the reactor. The valve on the output of the reactor can be closed for certain durations during the reaction as desired to apply a retention time factor to the reactor.

The nitrogen input is close to the base of the reactor, with nitrogen gas heated to reach the raw material. The raw material is placed on a perforated plate in the center of the reactor and the thermocouple is placed close to this level. Thus, this is aimed that the measured temperature is as accurate as the temperature of the raw material is exposed to. When the experimental results are compared with available literature information, it appears this aim was achieved.

Generally, ensuring the desired conditions for the reaction is related to the reactor and linked system. Additionally, when the necessary conditions are ensured, the reactor type or shape do not create a serious effect on the calorific values of the products [19,20].

To cool the gas phase products emerging from the reactor at temperatures of 250 ~ 400 °C, an inverse heat exchanger was used with total length of 5 meters. While cold water was transported into the heat exchanger from an external pipe, the products passed through the internal pipe and are cooled. The product output from the heat exchanger separates fluid and gas. It is important that the products emerge from the heat exchanger below 100 °C. The content of fluid pyrolysis products is close to the boiling point of water and material around 100 °C may be present [21].

Generally, with some limitations, a preliminary study of pyrolysis of impregnated paper waste was performed and the prepared pyrolysis experimental set allowing the possibility to research the topic with more advanced studies provided sufficient results for basic research.

5. Pyrolysis Results

Pyrolysis experiments were completed with the variables of temperature, retention duration and heating rate.

Waste impregnated paper (paper containing UF – MF resin) are vacuumed during the process and collected in small fragments in waste vessels. Considering the industrial pyrolysis process that may be applied in the future, the waste impregnated paper obtained for experiments was used without applying an additional fragmentation process. The dimensions of waste impregnated paper were mean 0.5 – 1 cm. Though there are relatively few larger pieces, these pieces were separated and raw material with appropriate mean size was chosen.

Numerous experiments have been carried out during the study, but only some remarkable resulted experiments have been explained for the sake of discussion.

The first experiment in the study loaded 30 g of waste impregnated paper into the reactor at room temperature and the reactor was heated to 400 °C. The heating process lasted 45 min and at the end of this process only solid and gas phase products were obtained.

The experiments focused on obtaining pyrolysis fluid in general and identifying the calorific value of pyrolysis fluid to get a measure about the energy efficiency. The absence of fluid products obtained from the first experiment revealed the need to change the temperature conditions primarily. When studies [22-25] about pyrolysis are investigated, it appears that pyrolysis processes with low temperatures and long durations mainly provide rich product composition in terms of solid phase (biochar).

Results related to the first experiment are given in Table 1.

Table 1. Product composition obtained from reactor heated from room temperature

Total product amount	Solid product	Fluid product	Gas product
30 g	25.1 g	0 g	4.9 g

In the second experiment where the reactor began heating and 30 g waste impregnated paper was loaded when the temperature was still 150 °C, fluid was obtained from the exchanger output with temperature at 300 °C (see Table 2). It took 20 minutes from the initial temperature to 300 °C with fluid flow observed. This is equivalent to a heating rate of nearly 7.5 °C. After 300 °C the fluid product was not obtained.

Table 2. Product amounts obtained from reactor heated to 150–300 °C

Total product amount	Solid product	Fluid product	Gas product
30 g	21 g	1.05 g	7.95 g

The reason for the lack of, or very low, fluid products in the results of the above experiments is due to carbonization. Carbonization, associated with slow pyrolysis, is a roasting process by taking humidity from the material in an inert atmosphere by applying a retention duration generally at 200-300 °C [24].

The experimental conditions and results mentioned above may be said to be similar to a carbonization or roasting process [26-28].

Biomass roasting processes are generally completed at temperature intervals of 200 – 300 °C with time intervals varying from half an hour to one and a half hours in an oxygen-free environment. Biomass roasting processes produce solid products with mainly stable characteristics [26]. As temperature increases, the quality of biochar (solid product) increases; however, there is information [29] stating that the amount of biochar may be consumed and reduce due to secondary reactions.

In the third experiment using waste impregnated paper with the same weight and color properties, the reactor output and nitrogen input were closed during the process with four minutes' retention time applied.

This experiment obtained fluid product output relatively more quickly and at lower temperature compared to the previous experiment. In the 18th minute with temperature of 265 °C fluid product was obtained and consequently 2.05 g of fluid product was obtained. After the output of fluid product, the temperature increase continued; however, in addition to obtaining combustible gas from the system output, there was no further fluid output. The results of this experiment provide an idea about the effect of retention time. The product combination from the third experiment is given in Table 3.

Table 3. Product composition from retention duration experiment

Total product amount	Solid product	Fluid product	Gas product
30 g	18.85 g	2.05 g	9.10 g

Application of retention duration, ensuring increased contact between volatile components within the reactor with biomass, generally causes an increase in fluid and gas product amounts. Together with the formation of long-chain components according to how long or short the retention time is, it is expected that such an application will increase fluid product amounts [29,30]. The obtained result supports the consideration of the effect of low temperature together with the increase in fluid product amounts with retention duration application.

There are studies [31,32] showing lengthened retention duration increases gas fluid amount while causing a reduction in fluid and solid product amounts. Accordingly, as the retention time increases, there is an increase in secondary reactions and as the degradation of volatile components within the reactor continues, the gas product amounts increase. Additionally, together with retention duration, high temperatures increase the gas amount in composition of pyrolysis products, lowering fluid and solid amounts [30,31].

The product composition percentages from the experiments mentioned above with the reactor heated from a certain temperature are given together in Table 4.

Table 4. Experimental results from defined temperature intervals

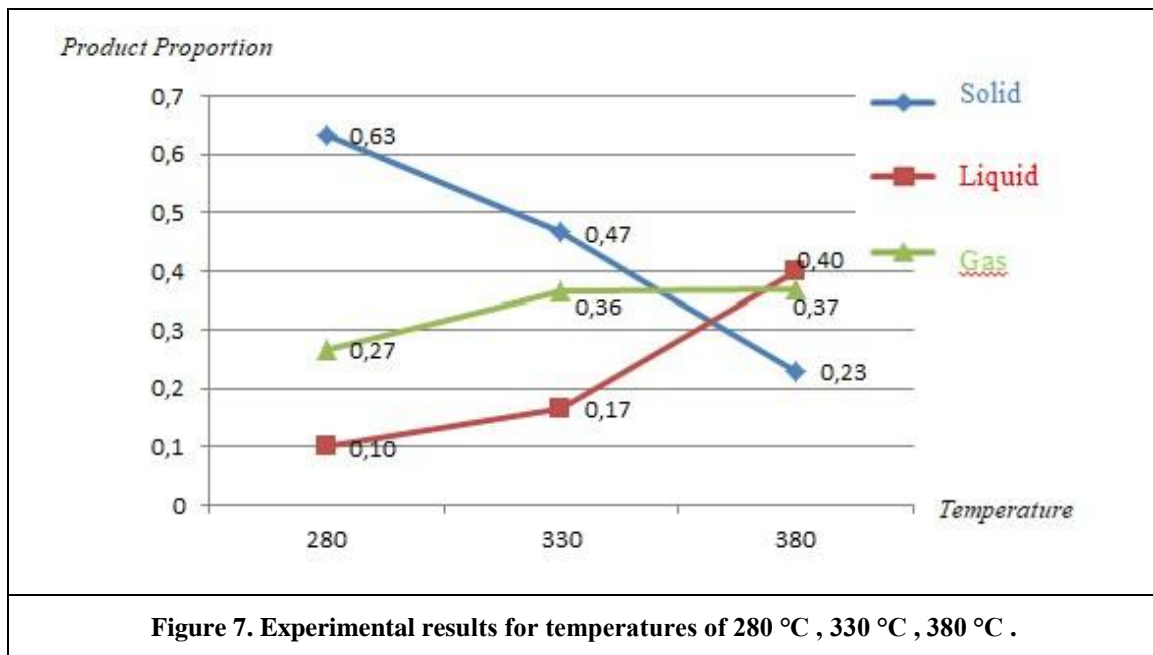
Order no.	Temperature interval	Solid product	Fluid product	Gas product
1	20 – 400 °C	84%	0%	16%
2	150 – 300 °C	70%	4%	26%
3	150 – 300 °C	63%	7%	30%

The reaction conditions and results from the experiments above identified that for reactions begun at low temperature reaching the temperatures where pyrolysis fluid is obtained takes a longer time and is equivalent to slow pyrolysis conditions. To complete the reaction more rapidly and to observe the effect of temperature difference on pyrolysis results independent of the effect of carbonization occurring at low temperature or slow heating rates, raw material was added directly to the reactor pre-heated to three different temperatures and pyrolysis was completed. As the reactor can be easily held at a fixed temperature for these experiments, 380 °C was determined as the highest temperature and 2 different lower temperature levels at 50 °C intervals were assessed.

To observe the pyrolysis results completed at three different temperatures, firstly the reactor was heated to these temperatures. When the desired temperature was reached, the reactor lid was opened and nitrogen flow begun while impregnated paper waste was loaded into the reactor and the lid closed. Thus, the aim was that waste impregnated paper reach the desired temperature rapidly. The results show that the temperature of waste impregnated paper within the reactor more rapidly increased compared to previous slow heating conditions and a process close to fast pyrolysis occurred.

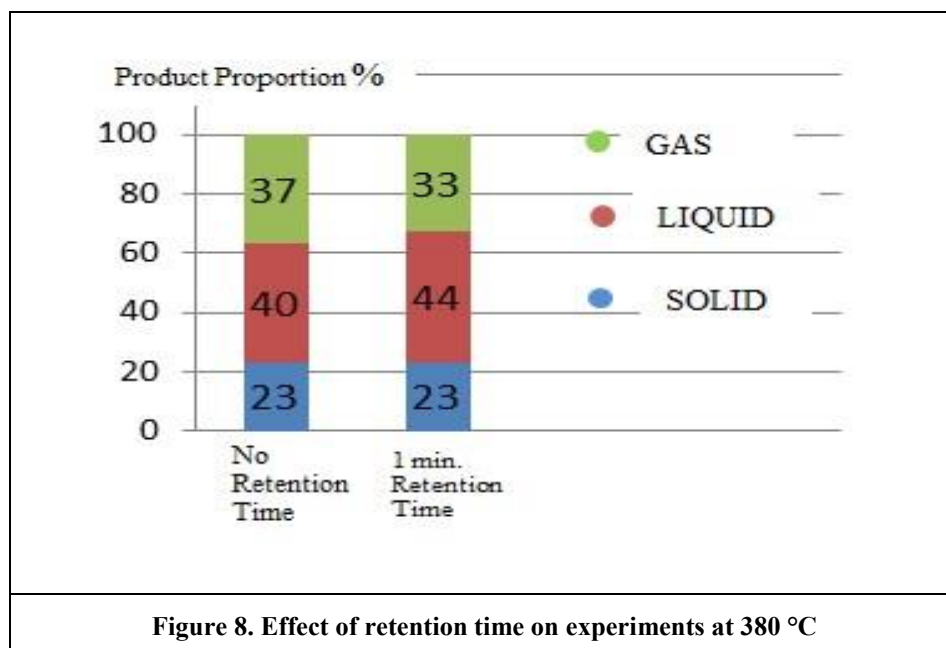
As seen in Figure 7, with the increase in temperature, there was a rapid reduction in solid product amounts. The gas proportion of products showed a visible increase with the first temperature difference, while fluid product amounts showed a more pronounced increase together with the temperature increase.

The waste impregnated paper has a composite characteristic. Firstly the UF and MF resins within the impregnated paper are exposed to a polymerization reaction. During the polymerization reaction, condensation occurs and polar molecules separate and this molecule is water [33,34]. Considering the pyrolysis reaction, at low temperatures UF and cellulose degradation may be mentioned [8,12]. Additionally, for thermal degradation of MF in the pyrolysis environment, temperatures of 300 °C and above may be more appropriate [11].



In light of the above information, it can be said that together with the increase in temperature, the heating rate that material is exposed to in the pyrolysis reaction is very effective on product composition. Some research related to pyrolysis of cellulose and cellulosic material found that, especially when temperatures below 600 °C are present, the gas and fluid product amounts increase, while solid product amounts reduce. Additionally, with the increase in temperature, there was an increase in gas amount in products, with a reduction observed in fluid amounts and the reaction tending toward gasification [2,5,35].

In addition to the effect of heating rate and temperature at 380 °C with highest fluid product yield, another experiment was completed to observe the variation to the product composition caused by application of retention time under the same conditions. The experimental results are shown in Figure 8.



As mentioned above, different applications of retention duration caused changes in the solid, fluid and gas product proportions. The retention time in the experiment was identified to increase the fluid amount in

products and reduce the gas amount. According to these results, it may be said that part of the gas phase is transformed into long-chain fluid structures during the retention time in the reaction environment.

Generally the effect of retention time is reported as long retention times at low temperatures increasing solid product amounts, long retention times at high temperatures increasing gas product amounts while short retention time at high temperatures increases fluid product amounts [36,37] Based on this, the retention time while the reaction continues may be said to influence the interaction of the solid, gas and product phases both with themselves and each other. The secondary reactions formed by the retention effect on gases forms more long-chain fluids which pass into the fluid phase.

At variable and fixed temperatures, the product amounts for experiments where the raw material is heated relatively more quickly are shown in Table 5. The results for experiment number 7 belongs to pyrolysis conditions with retention time applied. All of the experiments at fixed temperature had pyrolysis duration completed within 2 ~ 3 minute intervals.

Table 5. Pyrolysis results at fixed temperature and high heating rate

Experiment No	Temperature °C	Solid product %	Fluid product %	Gas product %
4	280	63	10	27
5	330	47	17	36
6	380	23	40	37
7	380	23	44	33

Another topic that is important in terms of the experimental results is the thermal (calorific) value of the fluid products obtained. This study only includes the thermal values for fluid products. Generally, it may be said that every phase of pyrolysis products has a notable thermal value [38-40].

The thermal values for fluid products obtained by pyrolysis reactions completed at three different temperatures are given in Table 6.

Table 6. Thermal values of pyrolysis fluids (Method TS 1740)

Sample	Reaction temperature (°C)	Thermal value (cal/gr)
1	280	3190
2	330	3850
3	380	4530

From the results observed in Table 6, it is understood that the thermal values of pyrolysis fluids increases together with the temperature increase. The increase in thermal value of pyrolysis fluids with increasing temperature is a known situation [41]. The thermal values of pyrolysis fluids are generally around half that of petrol products [42, 43]. Additionally, according to the raw material used in the pyrolysis reactions, situations where the thermal value approaches that of petrol products may be observed. For example, it appears the pyrolytic fluid thermal values of waste tires and some plastics approaches diesel fluid [44, 45]. The raw material used in the experiments in this study comprised paper and thermoset plastic material. There are studies [42,46] showing the pyrolysis fluid thermal values for paper were identified as 3150-3800 cal/g. A factor affecting thermal values of pyrolysis fluids is primarily water content in addition to the component properties of pyrolysis fluids [45, 47]. In addition to the water content of the raw material used, the water occurring during resin polymerization affects the content of the obtained fluid pyrolysis product.

The FTIR analysis of samples with the two highest thermal values revealed a concentration difference (see Figure 9). This is important in terms of the effect of water content on thermal value. The two samples had

similar peaks and analysis results showing 89.17% similarity were identified and are shown in Figure 9. The differences in height of similar peaks indicated concentration differences, with the highest line indicating a more concentrated structure; in other words representing the sample obtained at 380 °C. The results observed in this analysis show that samples from higher temperatures with higher thermal value at the same time are more concentrated. Considering that at higher temperatures, higher fluid product thermal values are obtained, these results are hopeful for future studies.

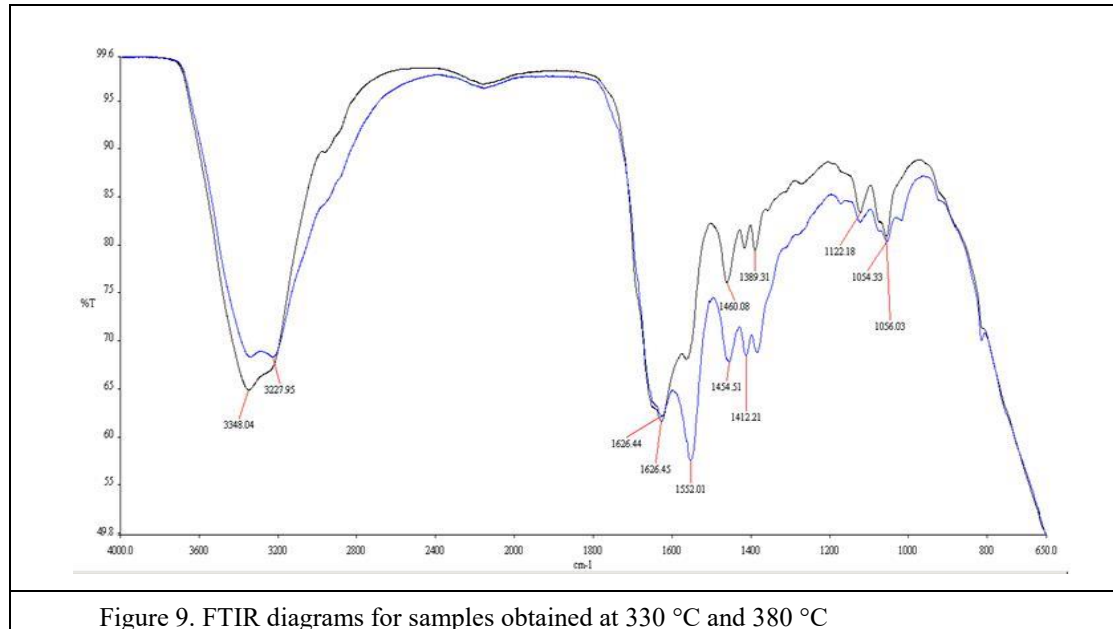


Figure 9. FTIR diagrams for samples obtained at 330 °C and 380 °C

6. Results and Discussion

The experiments and analyses performed have the quality of a preliminary study of the pyrolysis of waste impregnated paper from production within a limited industrial branch. With no previous study recorded, a type of feasibility study is presented showing initially whether the pyrolysis reaction is possible with impregnated paper, the product amounts obtained and the energy potential of products in terms of understanding or predicting based on data. This study attempted to find answers to certain questions about pyrolysis of waste impregnated paper, but was also performed to identify which questions should be asked about the topic and which answers require research.

Within this framework, the results of the study show that pyrolysis of waste impregnated paper is possible. The results of this pyrolysis process provided solid, fluid and gas products. It may be said that the fluid products obtained at available temperatures have notable thermal values (see Table 6).

Another element related to the study is whether the pyrolysis products of the hazardous waste of impregnated paper may be more useable in terms of environmental effects. Other data related to analysis results given in Figure 9 did not identify isocyanate, etc. compounds within pyrolysis fluids as a result of FTIR screening. Additionally, the result showing no cyanate compounds shows that these compounds are either not present or below a value of about 3%.

At higher temperatures than reached in this study, though theoretically more fluid product yield and higher thermal fuel values are expected, it should be considered that glycosyl groups forming during pyrolysis of cellulose in the alkali environment formed by UF resin may prevent disintegration of smaller structures among long-chain structures at high temperatures [48]. In research [9] about cellulose pyrolysis together with UF resin, though not using decor paper containing UF-MF due to direct impregnation processes, UF was reported to contribute to occurrence of carboxylic acids and water within the pyrolysis of cellulose. In view of

the fact that water is used to prevent pyrolysis [49], this can be evaluated together with the negative effect of pyrolysis of water mentioned in section 5. Thus, for future studies, the control of the amount of water in the system, before and during the pyrolysis will gain importance.

This preliminary research about the pyrolysis results of waste impregnated paper presents encouraging results for more comprehensive research.

In the context of the results obtained from the study, it may be said that research into optimum conditions in terms of energy and environmental safety of the solid, fluid and gas pyrolysis products from UF-MF resin paper waste will provide productive results in the future.

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