

The Effect of Catalyst on Bio-Oil Obtained from Fixed Bed Pyrolysis of Biomass Mixtures; a GC-MS Analysis

Kilincel Mert¹, Polat Fikret², Gunes Ebubekir Can³ and Toklu Ethem⁴

³Duzce University Engineering Faculty Mechanical Engineering Department, Turkey

Abstract

This study is focused on the effect of catalyst on quality and quantity of the products obtained from biomass using fixed bed pyrolysis reactor. In order to conduct this study two different biomass mixtures (including polymer and cellulose) were prepared. Also two different thermally activated catalysts (sepiolite and bauxite) were added both mixtures at 15% by mass. The heating rate of reactor was 5°C/min and the process temperature was 500 °C. In order to ensure inert atmosphere, the nitrogen gas was used at 20 ml/min flow rate. The reactor has an outlet which is connected to the atmosphere so the pressure of the vessel was equal to the ambient pressure. The formation of pyrolysis oil was investigated by GC-MS analysis. According to the results it can be concluded that, the presence of the catalysts increased the formation of the pyrolysis oil while decreased the char yield. The data obtained from the GCMS analyzer device library also show that the pyrolysis oil formula is ranging from C₇ to C₃₀. This is an indication that the catalysts used in the pyrolysis experiments lead to enhanced oil properties.

Keywords: pyrolysis, catalyst, biomass, GC/MS

Nomenclature			
<i>Sd</i>	<i>Sawdust</i>	<i>FM1</i>	<i>Mixture1 in fixed bed (no catalyst)</i>
<i>Wp</i>	<i>wood particles</i>	<i>FM2</i>	<i>Mixture2 in fixed bed (no catalyst)</i>
<i>Cb</i>	<i>cardboard</i>	<i>FMS1</i>	<i>Mixture1 in fixed bed (with sepiolite)</i>
<i>Pa</i>	<i>A4 paper</i>	<i>FMS2</i>	<i>Mixture2 in fixed bed (with sepiolite)</i>
<i>PC</i>	<i>polycarbonate particles</i>	<i>FMB1</i>	<i>Mixture1 in fixed bed (with bauxite)</i>
<i>PP</i>	<i>polypropylene</i>	<i>FMB2</i>	<i>Mixture2 in fixed bed (with bauxite)</i>
<i>LDPE</i>	<i>low density polyethylene</i>		
<i>HDPE</i>	<i>high density polyethylene</i>		
<i>Ct</i>	<i>cotton towel</i>		
<i>St</i>	<i>sepiolite</i>		
<i>Bt</i>	<i>bauxite</i>		

2nd International Conference on Research in Applied Science

30 October – 01 November 2019

Milan, Italy

1. Introduction

Biomass is one of the important renewable energy source that needs to be processed before utilized as a fuel. Various processing steps are necessary to convert raw biomass into useful energy using the three main processing technologies available: bio-chemical, thermochemical, and physio-chemical [1]. Pyrolysis is one of the main and prevalent thermochemical process to treat biomass. The process of pyrolysis can be defined as the chemical decomposition of organic matter by heat, in the absence of air, unlike the incineration methods [2]. Pyrolysis is the thermal degradation of macromolecules in the absence of air and generates oils and gases, which can be utilized for chemical applications or energy generation [3]. Additives can have a significant impact on the pyrolysis process. Catalysts are utilized to enhance the variety and quantity of liquid and gas end-products. Catalytic pyrolysis has been explored extensively for improving the quality of bio-oil and non-condensable gases. Many catalysts including natural and synthetic zeolites, and natural clays (bentonite, kaoline, cambrian clays, mergel clays, sepiolite and attapulgitite) have been investigated [4,5]. Also alumina based catalysts are used in some studies [6,7]. Studies showed that proper selection of the Si/Al ratio makes it possible to control the composition distribution, yields, and gasoline fractions of fuel.

The catalyst can promote decomposition reactions at low temperatures with lower energy consumption, reduced costs, increased the yield of products with higher added value, increased process selectivity, faster cracking reactions, leading to smaller residence times and reactors with smaller volumes, inhibiting the formation of undesirable products, inhibiting the formation of products consisting primarily of cyclic hydrocarbons, liquid products with a lower boiling point range [8]. In this study, catalysts of sepiolite and bauxite which has not been used commonly in catalytic pyrolysis.

Gas chromatography–mass spectrometry (GC-MS) is an analytical method that combines the features of gas-chromatography and mass spectrometry to identify different constituents within a sample [9]. Applications of GC-MS include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples. In this study GC-MS analysis is used for analyzing substances of pyrolysis oil for both catalytic and non-catalytic pyrolysis.

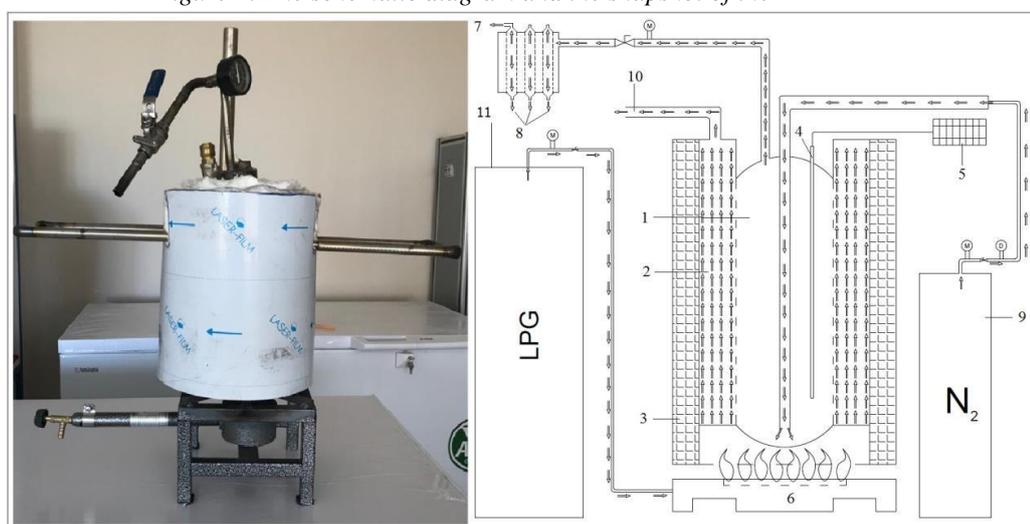
2. Methods

2.1 Experimental Setup

A laboratory-scale fixed bed pyrolysis reactor (FBR) was used in this study. The inner cylinder of the FBR, which constitutes the working volume of the unit, consists of 304 stainless steel sheet material of 114 mm diameter and 150 mm height and 7 mm thickness. In order to supply nitrogen to the system, a 5 mm diameter cylindrical pipe extending from the nipple to the base of the unit was added. The extension of the pipe to the bottom of the unit was also

made in order to ensure the inert atmosphere in the whole unit. A K-Type thermocouple connection was made for observe the temperature values during the process. Fig.1 shows the schematic diagram and the snapshot of the FBR. The numbers of the schematic diagram summarized as 1: pyrolysis vessel, 2: burning gas smoke exhaust path, 3: 50 mm glass wool insulation, 4: temperature sensor (K-type termokupl), 5: temperature data reader, 6: burner, 7: syngas exhaust, 8: pyrolysis oil outlet (condenser), 9: syngas outlet, 10: burning gas smoke exhaust, 11: LPG cylinder.

Figure 1: The schematic diagram and the snapshot of the FBR



2.2 Catalysts Preparation

Thermally activated sepiolite and bauxite were used as catalysts in the study. The catalysts were subjected to a series of treatments according to the ASTM D3943- 10 standards to activate them thermally. The catalysis were first treated with distilled water to remove any possible particles and contamination and mixed in a beaker at 280 rpm for 6 hours on an orbital platform mixer (Heidolph Unimax 1010). At the end of mixing process, specimens were filtered with 90 mm diameter, 2-4 μ m pore diameter under vacuum with slow filtration filter (FILTER-LAB 1244-90mm / Ø, 80g / m², 2-4 μ m porosity). The filtered samples were subjected to dehumidification at 105 ° C for 36 hours. Before starting the activation process, samples were taken from the oven and kept in the laboratory for 4 hours to reach room temperature. Dry samples reaching room temperature were mixed with 1 g of catalyst to 10 mL of 2M HCl acid solution in a beaker at 200 rpm. The solutions were then placed in a heated magnetic stirrer under a fume hood and left to be treated for 3 hours at 102 ° C. HCl acid treated products were removed from the mixer and allowed to cool. Samples which cooled to room temperature were repeatedly washed with distilled water until the filtrate was neutral in a buhner funnel placed on filter paper. The filtrate was measured with a pH meter and the process was terminated when

2nd International Conference on Research in Applied Science

30 October – 01 November 2019

Milan, Italy

the water was neutral. The filtered neutral samples were subjected to dehumidification at 104 ° C for 36 hours. The samples were calcined at 550 ° C in the muffle furnace for 2 hours and the thermal activation process was completed. After calcination process, samples were transferred to desiccator to prevent moisture catching and kept until the experiments were completed. Thermally activated catalysts were shown in Fig.2.

Figure 2: The snapshot of the catalysts



2.3 Biomass Preparation

Various polymeric and cellulosic materials were provided to realise experimental studies. These materials were provided from treated and untreated materials having polymeric and cellulosic properties. The treated materials (paper, cardboard, towel and wood) were prepared by cutting them in standard dimensions from the same group specimens. The untreated materials (PP, PC, HDPE, and LDPE) were supplied directly from the producers in granular form. Two different mixtures have been created by adding certain proportions of these materials (FM1, FM2). Afterwards, sepiolite and bauxite catalysts were added to these mixtures in 15% by weight and six different mixtures were obtained (FMS1, FMS2, FMB1, FMB2). Powdered sepiolite and bauxite samples were supplied as a catalyst in the experiments. The dimensional properties of the constituents that create mixtures are shown in Tab.1. On the other hand constituents of the mixtures are shown in Tab.2.

2nd International Conference on Research in Applied Science

30 October – 01 November 2019
Milan, Italy

Table 1: The dimensional properties of constituent of the mixtures

Constituent Name	Particle size of specimens
<i>Sd</i>	0.2-0.6 mm sawdust
<i>Wp</i>	10x 20 mm wood particles
<i>Cb</i>	10x 20 mm cardboard particles
<i>Pa</i>	10x 20 mm A4 paper particles
<i>PC</i>	2-3 mm granular polycarbonate particles
<i>PP</i>	3-4 mm granular polypropylene particles
<i>LDPE</i>	3-4 mm granular low density polyethylene particles
<i>HDPE</i>	3 mm granular high density polyethylene particles
<i>Ct</i>	10x 20 100% cotton towel
<i>St</i>	400-600 nm sepiolite particles
<i>Bt</i>	400-600 nm bauxite particles

Table 2: Constituent percentage of the mixtures

Constituent	Mass (%)	FM1 (%)	FM2 (%)	FMS1 (%)	FMS2 (%)	FMB1 (%)	FMB2 (%)
<i>Sd</i>	23.97	6.85	20.38	5.82	20.38	5.82	
<i>Wp</i>	31.51	31.5	26.78	26.78	26.78	26.78	
<i>Cb</i>	10.27	6.85	8.73	5.82	8.73	5.82	
<i>Pa</i>	10.27	3.42	8.73	2.91	8.73	2.91	
<i>PC</i>	3.42	10.27	2.91	8.73	2.91	8.73	
<i>PP</i>	3.42	10.27	2.91	8.73	2.91	8.73	
<i>LDPE</i>	3.42	10.27	2.91	8.73	2.91	8.73	
<i>HDPE</i>	3.42	10.27	2.91	8.73	2.91	8.73	
<i>Ct</i>	10.27	10.27	8.73	8.73	8.73	8.73	
<i>St</i>	-	-	15.00	15.00			
<i>Bt</i>	-	-	-	-	15.00	15.00	

All of the mixtures were prepared with precision scales (0.0001g sensitivity).

2nd International Conference on Research in Applied Science

30 October – 01 November 2019

Milan, Italy

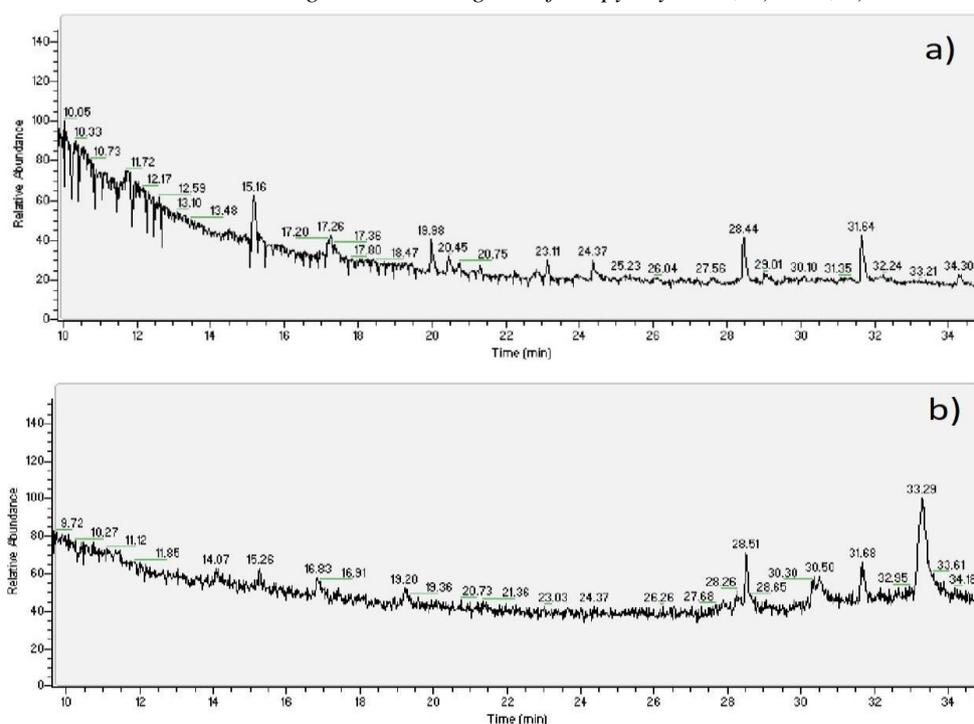
3. Results and Discussions

The fixed carbon and volatile content are components that directly affect the thermal value of the sample. The high volatile content (volatile matter; methane, hydrocarbons, hydrogen, carbon monoxide and carbon dioxide) indicates the presence of condensable and noncondensable gases when the fuel is heated.

GC-MS analysis of pyrolysis oil specimens was performed on Thermo Scientific GC-MS brand instrument. The peak values obtained from the instrument were automatically compared with the compounds recorded in the instrument's database. As a result, the program proposed the compounds that the peaks could belong to according to the time of occurrence of peaks and the area of projection with probability percentage.

Although pyrolysis oil was free from bitumen content and particles by using catalyst, it was diluted 1/50 in carbon disulphide (C₂S) solution and injected into GC-MS system for the device to give healthy results. During the GC-MS analysis, the analyses were repeated with standard methods with two different heating rates, dwell time and processing time and the same data were obtained. This is an indication that the analysis results are reproducible and reliable. Accordingly, the resulting compounds were noted in each analysis and are given in Fig.3, Fig.4 and Fig.5.

Figure 3: The diagram of the pyrolysis oil; a) FM1, b) FM2

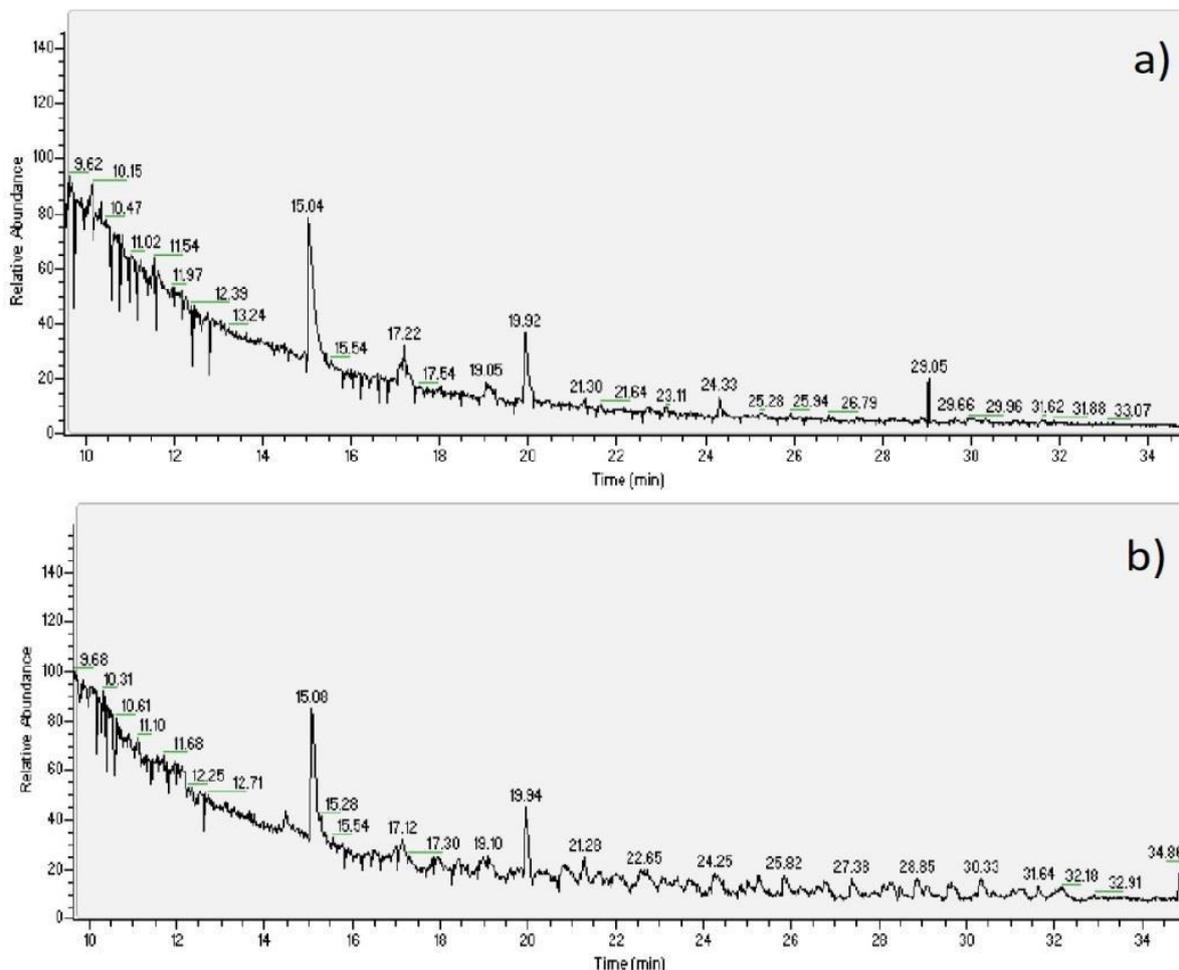


2nd International Conference on Research in Applied Science

30 October – 01 November 2019

Milan, Italy

Figure 4: The diagram of the pyrolysis oil; a) FMS1, b) FMS2
Figure 5: The diagram of the pyrolysis oil; a) FMB1, b) FMB2



According to the diagrams that GC-MS analyser creates based on its library, the possibilities of the material containing lists were given at Tab.3 and Tab.4. These results showed that FM-2, FMS-2 and FMB-2 pyrolysis oils were found to be the majority of volatile organics benzene as it expected. This is because these mixtures were cellulose rich mixtures. On the other hand, FM-1, FMS-1 and FMB-1 mixtures (which are polymer rich) pyrolysis oils were found to be predominantly hydroxyl acetaldehyde and acetic acid.

2nd International Conference on Research in Applied Science

30 October – 01 November 2019
Milan, Italy



Table 3: Compositions of polymer rich mixtures

No	Component name		
	FM-1	FMS-1	FMB-1
1	Hydroxy acetaldehyde	Hydroxy acetaldehyde	Hydroxy acetaldehyde
2	2-Cyclopenten-1-one	2-Cyclopenten-1-one	2-Cyclopenten-1-one
3	Di-methyl-heptane	Di-methyl-heptane	Di-methyl-heptane
4	Ethyl-benzene	Ethyl-benzene	Ethyl-benzene
5	Acetic acid	Acetic acid	Acetic acid
6	Cresol	Eugenol	Syringaldehyde
7	Eugenol	Naphthalene	Hydrochloride-propene
8	1,2,3-Trimethoxy-toluene	4-Allyl-2,6-dimethoxyphenol	2,6-Dimethoxy-phenol
9	Levogluconan	Furfural	Phenol
10	Furfural	Syringaldehyde	Furfural
11	Syringaldehyde	Cresol	Levogluconan
12	1,2,4-Trimethoxybenzene	2,6-Dimethoxy-phenol	Methyl-naphtalene
13	2-Methoxy-4-methyl-phenol	Levogluconan	Eugenol
14	2,6-Dimethoxy-phenol	1,2,4-Trimethoxybenzene	Naphthalene
15	Phenol	Methyl-naphtalene	Xylene
16	4-Allyl-2,6-dimethoxyphenol	Hydrochloride-propene	Styrene
17	3-Furanmethanol	Phenol	Biphenyl
18	2-Methoxy-phenol	Xylene	Fluorene
19	Xylene	Styrene	-
20	Styrene	-	-
21	α -methyl styrene	-	-
22	Methyl-naphtalene	-	-
23	Hydrochloride-propene	-	-

Table 4: Compositions of cellulose rich mixtures

No	Component name		
	M-2	MS-2	MB-2
1	Benzene	Benzene	Benzene
2	Di-methyl-heptane	Di-methyl-heptane	Di-methyl-heptane
3	Biphenyl	Styrene	Toulene
4	Fluorene	Naphthalene	1,4-Pentadiene
5	Styrene	Methyl-naphtalene	Indene
6	α -methyl styrene	Hydrochloride-propene	2-Ethylhexanal
7	Naphthalene	Toulene	Naphthalene
8	Methyl-naphtalene	1,4-Pentadiene	Methyl-naphtalene
9	Hydrochloride-propene	2,4-Hexadiene	Hydrochloride-propene
10	Toulene	1-Butene	Styrene
11	1,4-Pentadiene	Hydroxy acetaldehyde	2,4-Hexadiene
12	2,4-Hexadiene	Acetic acid	1-Butene
13	1-Butene	2-Ethyl-1-hexene	2-Ethyl-1-hexene
14	2-Ethyl-1-hexene	Indene	Hydroxy acetaldehyde
15	Indene	2-Ethylhexanal	Acetic acid

2nd International Conference on Research in Applied Science

30 October – 01 November 2019

Milan, Italy

16	2-Ethylhexanal	Ethyl-benzene	Ethyl-benzene
17	2-Ethyl-1-hexanol	Xylene	Xylene
18	Benzoic acid	Levogluconan	Levogluconan
19	Naphthalene	-	-
20	2-Methylnaphthalene	-	-
21	Acetic acid	-	-
22	Hydroxy acetaldehyde	-	-
<hr/>			
23	Levogluconan	-	-
24	Ethyl-benzene	-	-
25	Xylene	-	-

4. Conclusion

This study is about the effect of catalyst usage during the application of pyrolysis which is one of the thermal conversion methods on biomass. This experimental work indicates that presences of catalysts were positively affecting the pyrolysis oil formation. It can be clearly seen that the catalysts supplied mixtures have lower volatile organic compounds which means the catalysts creates advantages disposal of waste biomass via thermal treatment process.

Acknowledgment

The authors acknowledge the financial support from the DÜBAP-Duzce University Coordinatorship of Scientific Research Projects (Project No.: 2016.06.06.405; Project Title: Improvement of Gas Production and Energy Efficiency of a Municipal Solid Waste Thermal Processing Plant).

References

- [1] Thornley P., Adams, P., (2017). Greenhouse Gas Balances of Bioenergy Systems, Academic Press, Page: 107-13. ISBN: 978-008-101036-5
- [2] Reddy, P. J., (2002). Pyrolysis and Gasification Technologies in Energy Recovery from Municipal Solid Waste by Thermal Conversion Technologies, 1st ed. Pacific Grove, California, pp. 85-173.
- [3] Arvanitoyannis, I.S., (2008). Waste Management for the Food Industries.
- [4] Luque, R., Menéndez, J.A., Arenillas, A., Cot, J., (2012). Microwave-assisted pyrolysis of biomass feedstocks: the way forward? Energy Environ. Sci., vol 5, pp. 5481,
- [5] Pütün, E., Uzun, B.B., Pütün, A.E., (2006). Fixed-bed catalytic pyrolysis of cotton-seed cake: effects of pyrolysis temperature, natural zeolite content and sweeping gas flow rate Bioresour. Technol., vol. 97, pp. 701-710.
- [6] J.-L. Wang & L.-L. Wang (2011) Catalytic Pyrolysis of Municipal Plastic Waste to Fuel with Nickel-loaded Silica-alumina Catalysts, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 33:21, pp. 1940-1948.



2nd International Conference on **Research in Applied Science**

30 October – 01 November 2019

Milan, Italy

- [7] Murata, K., Brebu, M., & Sakata, Y. (2010). The effect of silica-alumina catalysts on degradation of polyolefins by a continuous flow reactor. *Journal of Analytical and Applied Pyrolysis*, 89(1), pp. 30-38.
- [8] Almeida, D., Marques, M. F., (2016). Thermal and catalytic pyrolysis of plastic waste. *Polímeros*, 26(1), pp. 44-51.
- [9] O. David Sparkman; Zelda Penton; Fulton G. Kitson (17 May 2011). *Gas Chromatography and Mass Spectrometry: A Practical Guide*. Academic Press. ISBN 978-008-092015-3