

The Catalytic Effects of Potassium Dichromate on the Pyrolysis of Polymeric Mixtures

Part I: Hazelnut Shell and Polyethylene Oxide and their Blend Cases

A. Caglar, B. Aydinli

Abstract—The pyrolysis of hazelnut shell, polyethylene oxide and their blends were carried out catalytically at 500 and 650 °C. Potassium dichromate was chosen according to its oxidative characteristics and decomposition temperature (500 °C) where decomposition products are CrO₃ and K₂CrO₄. As a main effect, a remarkable increase in gasification was observed using this catalyst for pure components and blends especially at 500 °C rather than 650 °C contrary to the main observation in the pyrolysis process. The increase in gas product quantity was compensated mainly with decrease in solid product and additionally in some cases liquid products.

Keywords—Hazelnut shell, Polyethylene oxide, Potassium dichromate, Pyrolysis.

I. INTRODUCTION

THE increasing energy demands which are based almost on oil resources and the irreversibility of these resources in comparison to life span of human beings necessitate the searching of alternative fuels not only due to their possible exhaustion in the near future, but also hazardous effects of byproducts on the environment.

Over the last decades there has been considerable research on renewable energy sources for the sake of preserving the environment in sustainable development. Pyrolysis differs from other recycling technologies in that converting especially waste materials into basic materials at directly atomic or molecular levels can be subsequently used for the production of alternative fuels or other precious chemicals by application of some refining processes [1]. Pyrolysis overwhelms other conversion processes for materials such as biomass, plastics, hazardous and municipal wastes, and in the case of inevitable mixtures of these materials due to mistreatment by governmental or local authorities. Neo reactor designs, operational conditions and catalysts are being continuously elaborated on and developed in order to obtain desired products from pyrolysis process. For several decades various types of physical and chemical recycling methods have been

elaborated on to convert wastes into useful materials ranging from recycled packaging materials to precious chemicals for the purpose of using them at any level of modern life.

Environmental impacts of wastes exert pressure on governments and researchers to conduct experimental investigations especially on polymeric wastes. Thermochemical conversions especially pyrolysis of biomass and polymer blends have been studied for a decade and they have steadily been increasing in recent years [2]-[4]. The interaction between biomass and polymeric materials which is called synergistic effect was tried to be propounded with kinetic analysis and product yield distribution by TGA and pyrolysis experiments in literature [5], [6].

Catalysts are groups of special materials in science and engineering in which their general effects decrease the time to reach equilibrium conditions [7]. But their values should not be underestimated because attaining an equilibrium condition without certain catalyst may take enormous amount of time. Sometimes the other catalytic effect of such special material was also mentioned which is totally different from the previous one. This behavior is that they may allow production of different products from the same reactants [8]-[13].

In this second case, catalysts should be called special chemical agents and some special attentions should be paid because the reaction pathway and mechanism and thus the obtained products can be totally different. To obtain desired products at relatively short time, various types of existing and synthesized catalysts should be chosen with a trial and error method probably in pilot plants. Catalysts in pyrolysis process may have more diverse effects on product files due to decrease in the selectivity of bond breakage and formation at higher temperatures. Generally, the catalysts used in pyrolysis process may be synthesized and they may be natural or based on inorganic materials, especially zeolites, transition metal oxides, halides and salts which can be porous and nonporous. It is assumed that porous catalysts are more effective than nonporous ones due to increased surface or other undetermined variables [14], [15].

K₂Cr₂O₇ is a common inorganic chemical reagent, most commonly used as an oxidizing agent in various laboratory and industrial applications. The Cr(VI) may form organometallic compounds which themselves catalyze the process at meta-stable hot melt composition during pyrolysis

A. Caglar is with the Science Education Department, University of Kastamonu, Kastamonu, CO 37200 Turkey (corresponding author to provide phone: +90-366 2142312; fax: +90-366 2123353; e-mail: atilacaglar@gmail.com).

B. Aydinli is with the Science Education Department, University of Kastamonu, Kastamonu, CO 37200 Turkey (e-mail: baydinli@gmail.com).

[16], [17].

In this study, in order to increase the interaction between hazelnut shell (HS) and polyethylene oxide (PEO) and also to obtain the desired product files $K_2Cr_2O_7$ catalyst was added in the pyrolysis medium. The pyrolysis of between HS, PEO, and their various mixtures with and without potassium dichromate were realized at 500 and 650 K. For each condition, solid, liquid and gas amounts were determined and compared to deduce the catalytic effect of especially potassium dichromate. Potassium dichromate which is not natural constituent of any plastic material or biomass was used in the pyrolysis of HS and PEO blends to change the amount of obtained products. It is well known that potassium dichromate is an oxidizing agent especially if it is coupled with acids and thus actually, Cr(VI) atoms binding to four oxygen atoms, in which two oxygen atoms bear (-1) formal charge, can act as a nucleophile and Cr atom can act as an electrophile. These can easily activate especially π -bonds and also vulnerable σ -bonds, raising C bonds breakage significantly [18].

Reactions of hydrocarbons with metal complexes exhibit some common features where abstraction of a hydrogen atom from hydrocarbon by metal-oxo complexes is a key step, leaving intermediate alkyl radicals at room conditions. With increased temperature in the pyrolysis process, this extra rendering capability of radical formation may result in enormous chain reactions which yield extra amount of gas products [16], [19], [20].

II. EXPERIMENTAL

A. Materials and Catalyst

HS powder having 40 mesh aperture was dried at 30 °C in the oven for 24 hours and it was used in the pyrolysis experiments. Some of its physical and chemical properties were supplied before and also given here in Table I. Hazelnut is an important biomass resource of Turkey and its shell is a by-product of nut processing factories in the East Black Sea Region of Turkey. Annual hazelnut production of Turkey is approximately 500 000 tons and half of this is shell. HS has considerably high HHV; 18.9 MJ/kg [3].

PEO sample was supplied by Aldrich ($M_w = 4$ million) in granule form and was used as supplied. The general structure of PEO's is $\{-CH_2 - CH_2 - O-\}$. They are hydrophilic and of low melting point of approximately 65 °C. Pyrolysis of PEO produces generally vinylic and cyclic ethers at low molecular weights, hydroxyls compounds and hydrogen [21], [22].

$K_2Cr_2O_7$ is supplied as red-orange crystalline solid powder, having apparent density of 2.0 g/cm³ and bulk density of 2.7 g/cm³. Its melting point is 398 °C and it decomposes at 500 °C, yielding CrO_3 and K_2CrO_4 [23].

TABLE I
THE PROXIMATE AND ULTIMATE ANALYSIS OF HS

Proximate analysis (wt %)	
Moisture	9.2
Ash	1.3
Extractives (Alcohol-Benzene)	3.4
Lignin	42.5
Cellulose	25.9
Hemicelluloses	28.9
Fixed Carbon	19.5
Volatile	70.0
Elemental analysis (wt %)	
C	51.5
H	5.2
O	43.2
N	0.2
Higher Heating Value (MJ/kg)	18.9

B. Pyrolysis

The experiments were performed at 500 and 650 °C at various compositions of HS, PEO and $K_2Cr_2O_7$, and sample sets were given in Table II.

TABLE II
THE AMOUNT OF CONSTITUENTS IN SAMPLE SETS

Sample sets	Constituents amounts (g)		
	HS	PEO	$K_2Cr_2O_7$
1.00	0.00	0.0	
0.00	1.00	0.0	
1.00	0.00	0.5	
1.00	0.00	1.0	
0.00	1.00	0.5	
0.00	1.00	1.0	
1.00	1.00	0.0	
1.00	1.00	0.5	
1.00	1.00	1.0	
1.50	0.50	0.0	
1.50	0.50	0.5	
1.50	0.50	1.0	

The residence time of each pyrolysis experiment is adjusted for 15 minutes. Liquids were determined by subtracting weights of apparatus parts before and after the pyrolysis runs. Char amount was weighted directly. Gas product was found by difference.

C. Setup

The pyrolysis experiments set up were given in Fig. 1. The stainless-steel tubular reactor after doped with samples was inserted in electrical furnace at 500 or 650 °C and connected with vessel to liquid collecting tubes that was embedded in salty ice. Char products were retained in reactor chamber.

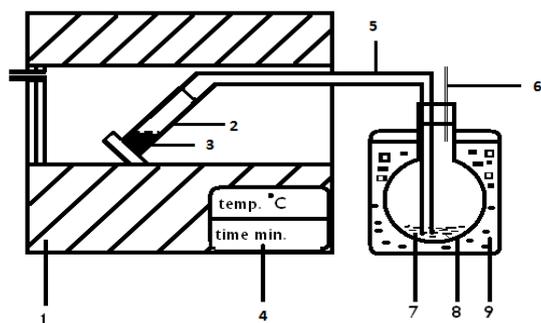


Fig.1 Experimental setup: 1) Electrical furnace, 2) Tubular reactor, 3) Sample, 4) Control Panel, 5) Connecting vessel 6) Gas outlet
7) Liquid, 8) Liquid collecting vessel, 9) Salty ice.

III. RESULT AND DISCUSSION

In this study, the catalytic effect of potassium dichromate on the pyrolysis products amounts of pure HS and PEO, and their blends were examined at 500 and 650 °C. Just solid, liquid, and gas amounts were found gravimetrically. Interestingly, non-linear catalytic effect was observed on pure components and their blends. Even though any chromatographic and spectroscopic analysis were not performed, the obtained results here obviously are valuable and promising enough to conduct further analysis to determine product files. It can be assumed that the catalytic effect of potassium dichromate is different for HS, PEO and their blends. The detailed results and data are as follows:

A. The Amounts of the Pyrolysis products; catalytic and non-catalytic

The solid, liquid and gas products amounts obtained from the pyrolysis of pure HS, PEO and their blends with and without catalyst at 500 and 650 °C were given in Figs. 2, 3 and 4 separately. Pure HS generates high amount of solid products and addition of potassium dichromate suppresses it substantially from 38 % to 15 % for 500 °C and similarly, but less pronouncedly for 650 °C (Fig. 2). If lower amount of solid product is aimed, instead of increasing temperature, usage of a catalyst may be energy saving choice when the price of catalysts takes priority. This result surprisingly shows that the fixed carbon content of HS is probably converted into low molecular weights products such as CO₂, CO or other carbonaceous chemicals. The pure PEO actually did not produce considerable amount of solid products, but the addition of 0.5 g potassium dichromate, yielding 3 % solid product. In the case of the blends, higher amount of solid products were obtained with or without catalyst than mathematical average of pure HS and PEO. This shows that the pure constituents increase their stability themselves, but the addition of potassium dichromate decreases the stability a little bit but not vanishes completely. Throughout all the experiments, normally solid product amount is lesser at 500 °C than 650 °C. In brief, potassium dichromate is very effective

in altering the solid product amount; probably due to C-C bond rupturing by the attack of oxygen atoms in potassium dichromate.

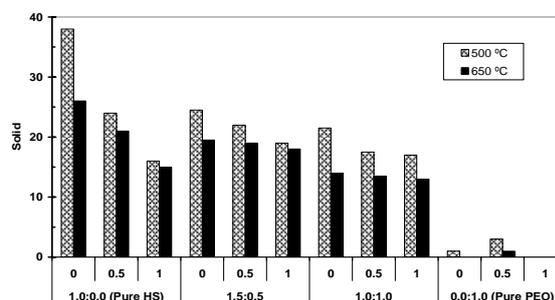


Fig. 2 The solid product amounts from pure and K₂Cr₂O₇ added HS and PEO, and their two blends at two temperatures

The additions of potassium dichromate caused a decrease in liquid products amounts in all samples except for pure HS (Fig. 3). Generally, liquid product amounts at 650 °C are higher than the amounts at 500 °C. The liquid products obtained from blends are consistent with mathematical averages of pure ones. But 1 g addition of potassium dichromate to PEO decreased the liquid product amount significantly. Probably, the breakages of C-C bonds in PEO by potassium dichromate cause catastrophic degradation of PEO, which produces CO and CO₂ latently.

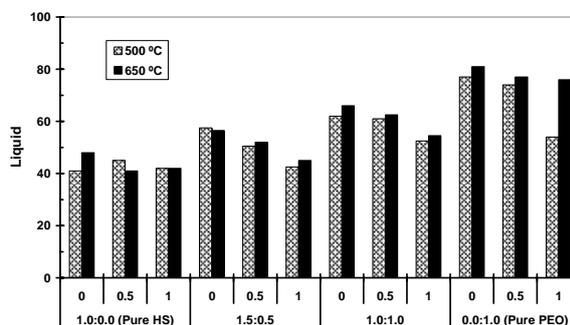


Fig. 3 The liquid product amounts from pure and K₂Cr₂O₇ added HS and PEO, and their two blends at two temperatures

The real interesting results lie in the gas products amount distribution (Fig. 4). It can be definitely stated that potassium dichromate has significant gasification effect on the pyrolysis of mentioned materials. With an increase in potassium dichromate amount in the pyrolysis of pure HS, the gas product amounts increased from 20 to 40 % approximately. In terms of ratio, it almost doubles for both temperatures. The increase of catalyst amount from 0.5 g to 1.0 g in the pure HS, the gas product amount became almost equal for the two temperatures. This may show that there are competing reactions in the scarcity of potassium dichromate at lower amounts of it. The pyrolysis reactions, in which temperatures

are relatively high, can be very much different from normal temperature reactions, because the ratio of reacting molecules having enough energy at pyrolysis temperatures can reach almost unity. Thus, the amount of reactants play a critical role and some of them may be limiting reactants according to compositions. Another interesting observation goes to the pyrolysis of pure PEO at 500 °C with 1.0 g potassium dichromate where the gas product amount doubled the result at 650 °C which is an unexpected result with increase in temperature. Since the decomposition temperature of potassium dichromate is 500 °C and while it decomposes into CrO_3 and KCrO_4 which are less reactive than nascent $\text{K}_2\text{Cr}_2\text{O}_7$, the oxygen atom at break point continuously reacts with carbon bonds on the PEO chains. It seems that $\text{K}_2\text{Cr}_2\text{O}_7$ is a limiting reactant if it is 0.5 g in 1 g PEO. 1.5:0.5 blend with 1.0 g $\text{K}_2\text{Cr}_2\text{O}_7$ at 650 °C produced the highest gas amount (47 %) which is also greater than the pure components. If an increase in gas product amount is aimed at, that point seems very suitable.

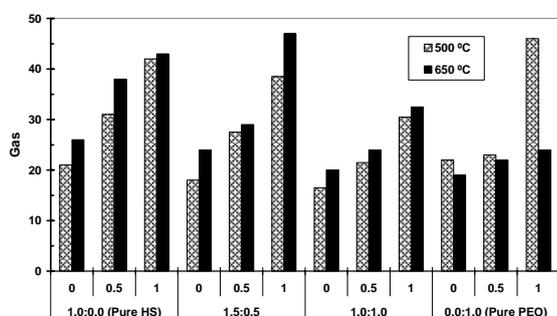


Fig. 2 The gas product amounts from pure and $\text{K}_2\text{Cr}_2\text{O}_7$ added HS and PEO, and their two blends at two temperatures

B. Intra-converting of the pyrolysis products with the effect of the catalyst amount and temperature

For pure HS, with an increase in the catalyst amount, solid product is converted into gas products with little fluctuation in liquid product at 500 °C (Fig. 5). Before discussing the pure PEO where the situation is clear, primarily blends should be discussed contrary to the pure HS, in which the increase of gas product amount is due to the conversion of the liquid product into the gas. This difference stems from triple synergy of the components. The similar observations can be alluded for 650 °C but less profoundly (Fig. 6). The gasification effect of potassium dichromate at 500 °C is higher than that at 650 °C. This is against the general characteristics of pyrolysis reactions [24]. Here, it may be due to the coupling of the decomposition of potassium dichromate and the pyrolysis process at the same temperature of 500 °C. This temperature is a border line of potassium dichromate in keeping the structure in the highest activity after which it decomposes into less reactive chemicals, CrO_3 and K_2CrO_4 .

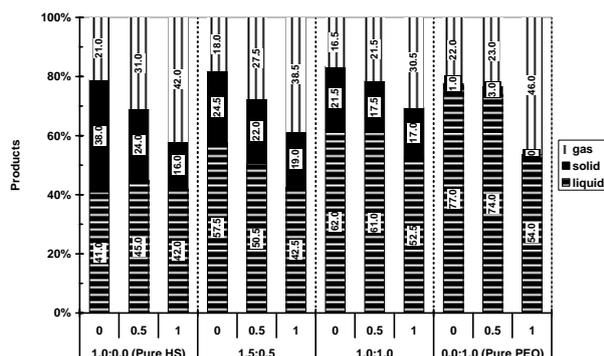


Fig. 5 The solid, liquid and gas product amounts from pure and $\text{K}_2\text{Cr}_2\text{O}_7$ added HS and PEO, and their two blends at 500 °C

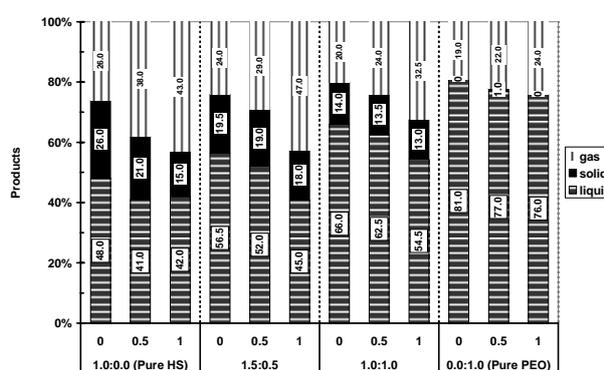


Fig. 6 The solid, liquid and gas product amounts from pure and $\text{K}_2\text{Cr}_2\text{O}_7$ added HS and PEO, and their two blends at 650 °C

IV. CONCLUSION

The main conclusion without doubt is an unexpected enormous gasification effect of potassium dichromate on the pyrolysis of pure HS, PEO and their blends especially at 500 °C. Normally, the induction of several percentages of variation in products amount in pyrolysis processes due to catalyst is considered to be promising for further studies. Here the intra-conversion of the solid and/or liquid products into the gaseous materials is between 5 to 20 %. This much increase in the gas amounts strongly imply the gaseous species change due to some probable change in reaction mechanisms. This can just happen with the breakages of more and more carbon-carbon and carbon-oxygen bonds with an increase in the catalyst ratio.

The second important derived result is that the decomposition of potassium dichromate at 500 °C reversed the temperature effect on gas product generation. Therefore, the decomposition or any crystal structure change of the so-called catalyst with temperature should be considered to obtain their desired effects on the pyrolysis medium.

The addition of PEO in HS favored liquid production compared to rational mathematical sum from pure components. But the addition of catalyst to the blends

increased the gas product at the expense of liquid and also solid residue.

The real purposes of these kinds of studies are to find some ways to utilize the so-called environmental pollutant materials for both acquisition of stored energy in them and cleaner environment.

REFERENCES

- [1] T. P. Williams, N. Nugranad, "Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks," *Energ.* Vol. 25, no. 6 pp. 493-513, Jun. 2000.
- [2] S.M. Al-Salem, P. Lettieri, J. Baeyens, "Recycling and recovery routes of plastic solid waste (PSW): A review," *Waste Manage.* Vol. 29, no. 10, pp. 2625-2643, Oct. 2009.
- [3] A. Caglar, B. Aydinli, "Isothermal co-pyrolysis of hazelnut shell and Ultra-High Molecular Weight Polyethylene: The effect of temperature and composition on the amount of pyrolysis products," *J. Anal. Appl. Pyrol.* Vol. 86, no. 2, pp. 304-309, Nov. 2009.
- [4] A. Aboulkas, K. El Harfi, M. Nadifiyine, A. El Bouadili, "Thermogravimetric characteristics and kinetic of co-pyrolysis of olive residue with high density polyethylene," *J. Therm. Anal. Cal.* Vol. 91, no. 3, pp. 737-743, Mar. 2008.
- [5] A. Jimenez, R. A. Ruseckaite, "Binary mixtures based on polycaprolacton and cellulose derivatives," *J. Therm. Anal. Cal.* Vol. 88, no. 3, pp. 851-856, Jun. 2007.
- [6] P. Grammelis, P. Basinas, A. Malliopoulou, G. Sakellaropoulos, "Pyrolysis kinetics and combustion characteristics of waste recovered fuels," *Fuel*, vol. 88, no. 1, pp. 195-205, Jun. 2009.
- [7] A.E. Shilov, G.B. Shul'pin, "Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes" *Catalysis by Metal Complexes*, Edited by B.R. James. Kluwer Academic Publishers, USA, pp. 1-19 2000.
- [8] Y.Wan, P.Chen, B. Zhang, C. Yang, Y. Liu., X. Lin, R. Ruan, "Microwave-assisted pyrolysis of biomass: Catalysts to improve product selectivity," *J. Anal. Appl. Pyrol.* Vol. 86, no. 1, pp. 161-167, Sep. 2009.
- [9] J. Shie, J. Lin, C. Chang, S. Shih, D. Lee, C. Wu, "Pyrolysis of oil sludge with additives of catalytic solid wastes," *J. Anal. Appl. Pyrol.* Vol. 71, no. 2, pp. 695-707, Jun. 2004.
- [10] J.M. Encinar, J.F. González, G. Martínez, S. Román, "Catalytic pyrolysis of exhausted olive oil waste," *J. Anal. Appl. Pyrol.* Vol. 85, no. 1,2, pp. 197-203, may. 2009.
- [11] A. Khelfa, V. Sharypov, G. Fingueneisel, J. V. Weber, "Catalytic pyrolysis and gasification of *Miscanthus Giganteus*: Haematite (Fe_2O_3) a versatile catalyst," *J. Anal. Appl. Pyrol.* Vol. 84, no. 1, pp. 84-88, May. 2009.
- [12] K. Bru, J. Blin, A. Julbe, G. Vole, "Pyrolysis of metal impregnated biomass: An innovative catalytic way to produce gas fuel," *J. Anal. Appl. Pyrol.* Vol. 78, no. 2, pp. 291-300, Mar. 2007.
- [13] H. Zhang, R. Xiao, H. Huang, G. Xiao, "Comparison of Non-Catalytic Fast Pyrolysis of Corn cob in a Fluidized Bed Reactor," *Bioresour. Technol.* Vol. 100, no. 3, pp. 1428-1434, Feb. 2009.
- [14] E. Putun, B. B. Uzun, A.E. Putun, "Fixed-bed catalytic pyrolysis of cotton-seed cake: Effects of pyrolysis temperature, natural zeolite content and sweeping gas flow rate," *Bioresour. Technol.* Vol. 97, no. 5, pp. 701-710, Mar. 2006.
- [15] M. Chen, J.Wang, M. Zhang, M. Chen, X. Zhu, F. Min, Z. Tan, "Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating," *J. Anal. Appl. Pyrol.* Vol. 82, no. 1, pp. 145-150, May 2008.
- [16] Q. Fu, D. S. Argyropoulos, D. C. Tilotta, L. A. Lucia, "Understanding the pyrolysis of CCA-treated wood: Part I. Effect of metal ions," *J. Anal. Appl. Pyrol.* Vol. 81, no. 1, pp. 60-64, Jan. 2008.
- [17] Shilov, A.E., and Shul'pin, G.B., 2000. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes. Catalysis by Metal Complexes*. Edited by B.R. James. Kluwer Academic Publishers, USA, pp. 318-363.
- [18] M. Nishimura, S. Iwasaki, M. Horio, "The role of potassium carbonate on cellulose pyrolysis," *J. Taiw. Inst. Chem. Engineer.* Vol. 40, no. 6, pp. 630-637, Nov. 2009.
- [19] O. Ioannidou, A. Zabaniotou "Agricultural residues as precursors for activated carbon production—A review" *Renew. Sustain. Energ. Rev.* Vol. 11, no. 9, pp. 1966-2005, Dec. 2007.
- [20] Y.Wan, P.Chen, B. Zhang, C. Yang, Y. Liu., X. Lin, R. Ruan, "Microwave-assisted pyrolysis of biomass: Catalysts to improve product selectivity," *J. Anal. Appl. Pyrol.* Vol. 86, no. 1, pp. 161-167, Sep. 2009.
- [21] Z. K. Lin, S.F. Li, "Effects of nano nickel powders addition on flash pyrolysis of poly(ethylene glycol)," *Eur. Polym. J.* vol. 44, no. 3, pp. 645-652, Mar. 2008.
- [22] B. Aydinli, A. Caglar, "The comparison of hazelnut shell co-pyrolysis with polyethylene oxide and previous ultra-high molecular weight" *J. Anal. Appl. Pyrol.* Vol. 87, no. 2, pp. 263-268, Mar. 2010. http://en.wikipedia.org/wiki/Potassium_dichromate
- [23] Basak Burcu Uzun, Ayse Eren Pütün, Ersan Pütün, "Fast pyrolysis of soybean cake: Product yields and compositions," *Bioresour. Technol.* Vol. 97, no. 4, pp. 569-576, Mar. 2006.