

# H<sub>2</sub> Production Improvement during Pyrolysis Catalized by Zeolites

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The aim of this study is to enhance the yield of H<sub>2</sub> during pyrolysis of waste lubricant oils using Na-Y zeolite as catalyst. The pyrolysis at high temperature (lower than 700°C) of recycled lubricant oils was successfully carried out under a nitrogen atmosphere. Different techniques were used for zeolite characterization: transmission electron microscopy (TEM), Raman and FT-IR spectroscopy, X-ray diffraction and N<sub>2</sub> adsorption-desorption analyses. The results of the catalytic tests show that the average concentration of H<sub>2</sub> produced during pyrolysis increases with respect to untreated (without zeolite), i.e. our zeolite Na-Y catalyst favors H<sub>2</sub> formation. Moreover, the total yield of all gas species is increased in presence of the Na-Y zeolite catalyst.

## 1. Introduction

Biomass is considered a renewable source and an alternative resource to the fossil fuels for the production of energy and chemicals. Waste oils is a kind of biomass that refers to contaminated or degraded liquid products, mainly consisting of waste lubricating oil coming from machinery and cooking oil. Waste lubricating oil is derived from engine oil, transmission oil, hydraulic and cutting oils (Whisman et al. 1978 and Arpa et al., 2010), whereas waste cooking oil is originated from biological resources such as coconut, sunflower, soybean, palm tree, cottonseed, rapeseed and olive. Waste oils are well-known hazardous materials, because of the presence of degraded additives and undesired substances, that could cause adverse impacts to the human health and the environment. In 2010, the global consumption of lubricating oils was approximately of 42 million tons (International Environmental Technology Centre (IETC), 2013). In particular, about 50% of the lubricating oil resulted in the generation of 20 million tons of waste oil (International Environmental Technology Centre (IETC), 2013). Moreover, waste cooking oils are additional discarded oils in huge amount. Therefore, the management of waste oils is one of the major environmental concerns in modern society. The disposal of waste oils is a new challenge, as the improper disposal of this hazardous waste can generate direct problems to human health. The development of an environmentally safe, sustainable, socially acceptable, and cost-effective solution should be taken into primary consideration for the treatment, recovery, and disposal of waste oil (Stehlik, 2009). There are some processes, (e.g. transesterification, hydrotreating, gasification, membrane technology and solvent extraction), that have been exploited in order to tackle the problem derived from the disposal of waste oil and to formulate the feasibility and sustainability of waste to energy conversion (Yaman, 2004; Rostrup-Nielsen, 2005 and Dodds et al., 2007). However, it was found that current technologies for treatment and recycling of waste oils are still far from being technically and economically feasible versus eco-friendly and sustainable approaches. Thus, an alternative technology should be developed in order to effectively treat and recycle waste oils by transforming them into high value-added materials.

Although the use of pyrolysis (Arregi et al. 2015 and Peres et al., 2013) is not widespread as yet, this technique has recently shown to be a potential alternative to convert waste oils into useful fuel products and chemical feedstock. Pyrolysis shows great potential in this field, because of: (i) high feedstock flexibility; (ii) simple and inexpensive system; and (iii) ability to work "in loco". Pyrolysis is defined as a heat promoted chemical decomposition, and generally refers to the chemical decomposition of organic materials heated in an

environment with an insufficient supply of oxygen for combustion. Waste oils can be reconstructed chemically by heating in an oxygen-free environment. Pyrolysis process promotes “waste to energy” conversion (Peres et al., 2013), which is an energy recovery application (Arregi et al. 2015) that employs processing technologies to produce energy or valuable materials from waste materials. The pyrolysis process allows to reuse oils as a resource and sell it as a new product. There has not been a consensus on which is the main pyrolytic product, since various observations were reported by researchers and these could be accounted by factors derived from the waste composition and experimental conditions (e.g. reaction temperature, vapour residence time, and heating rates), (Bridgwater, 2012; Sinač et al., 2010). In general, pyrolysis produces three classes of products, namely: solid char residues, waxy liquid oil compounds, and gases. Pyrolysis has not been fully exploited for the treatment of waste oils. On the other hand, it has been received considerable attention for the production of energy-dense products from waste materials (Fernandez et al., 2011). Pyrolysis has certain advantages over other treatment methods for waste disposal (Arpa et al., 2010). The most crucial advantage is that it does not pollute the environment when performed appropriately, because all pyrolysis products such as gases, oils, and carbonaceous residues can be used as fuels. However, pyrolyzed oil can be polymerized again because it consists of many unsaturated hydrocarbons (Arpa et al., 2010). The process can be optimized to maximize production of any of these constituents by altering parameters such as process temperature and reactant residence time (Onwudili et al., 2009), e.g. the production of gases can be improved by increasing temperature and residence time.

In particular, the main gases produced by pyrolysis consist of  $H_2$ ,  $CH_4$ ,  $CO$  and  $CO_2$ .

The use of catalysts or additives during pyrolysis process is gaining increasing interest. Catalytic pyrolysis has shown advantages over non-catalytic reaction (Bu et al., 2014; Kuan et al., 2013; Yu et al., 2014). The use, in the pyrolysis processes, of catalysts or additives to improve the yield or quality of gaseous or liquid fuels from biomass, is still in its infancy. Thus, it is envisaged that different catalysts (Nokkosmaki et al., 2000) could be studied and utilized in the pyrolysis of waste oils in order to develop a catalytic system suitable for waste oil recovery. The use of solid catalysts to facilitate pyrolysis has been previously reported. In particular, the product selectivity has been found strongly affected by the presence and nature of heterogeneous catalysts, water steam and gas feed nature (Lima et al., 2004).

Zeolites can be used as catalyst (Sarno et al., 2004) to improve the product selectivity in a pyrolysis process, e.g. increasing the recovery of oil or gaseous product from pyrolysis process, reducing energy consumption and polluting emissions (Wan et al., 2009 and Zuo et al., 2011). In particular, zeolites, aluminosilicate minerals, are made of three-dimensional networks that preferentially absorb molecules and exclude larger ones. Zeolites are considered nanomaterials because of their pore sizes that range from approximately 0.4 to 1 nm. They excel in catalytic processes starting from petroleum feedstock because of: their strong tunable acidity; microporosity (< 2nm, either in 1, 2 or 3D), which allows molecular traffic control and high reaction surface areas; their robustness and high thermal stability, leading to easy regeneration at elevated temperatures; and finally, their adjustable nature so that they match the need of the desired chemical transformation. Each nanoporous materials has the potential to offer unique structural and chemical features that can be beneficial for an industrial application. As a result of their high surface areas, nanoporous catalysts contain a high density of active sites, which can be directly involved in the reaction at a molecular level. This characteristic results in enhanced activity, and thus a more effective catalytic system. For zeolites, the ability to exchange cations is another essential feature for applications in catalysis.

Recently, there has been a great deal of interest in another aspect of zeolites, the primary crystal size, which can be potentially exploited in nanotechnology. Nanocrystalline zeolites are zeolites with discrete, uniform crystals, with dimensions of less than 100 nm, that have unique properties relative to conventional micrometer-sized zeolite crystals. Nanocrystalline zeolites have higher external surface areas and reduced diffusion path lengths relative to conventional micrometer-sized zeolites, which make them promising catalytic materials and adsorbents.

Among zeolites, Y zeolite (Sarno et al., 2004) is a solid acid catalyst with a FAU type framework topology. It features three-dimension pore channels with SOD cages and possesses highly stable crystalline framework with a large pore opening of 0.74 x 0.74 nm (Shi et al., 2013). Micropores structure provides large surfaces, strong acid sites, especially, excellent shape selectivity for zeolite Y.

Catalytic pyrolysis of waste lubricating oil in the presence of nanocrystalline (Na) zeolite in the form Y, (Na-Y), has been carried out in this study to investigate its ability to improve hydrogen amount in the produced gas. The presence of the zeolite Na-Y, which serve as catalysts for the pyrolysis process, allows obtaining a very high carbon conversion and a gaseous product mainly consisting of  $CO$  and  $H_2$ .

## 2. Experimental Section

### 2.1 Biomass and chemicals

Waste motor oil (WM) (S: 0.31 wt%, Cu: 15.4 mg/kg, Ni: 0.874 mg/kg, Cr: 0.874 mg/kg, Cd: 0.485 mg/kg, Zn: 403 mg/kg, Pb: 5.63 mg/kg, Hg: 0.083 mg/kg, and As: 0.821 mg/kg) was used without purification. Sodium hydroxide (NaOH) pellets, tetraethoxysilane (TEOS), aluminium iso-propoxide (AIP), tetramethylammonium hydroxide (TMAOH, 25% aq.), were purchased from Merck.

### 2.2 Preparation of zeolite Na-Y catalyst

The preparation of the solution for nanocrystalline zeolite Na-Y synthesis followed the method reported in (Mintova et al., 1999; Larlus et al., 2006). Tetramethylammonium hydroxide solution and aluminium isopropoxide were added to a solution of NaOH 0.05 N in deionized water and stirred vigorously until the solution became clear. The mixture so obtained added with Tetraethylorthosilicate ( $0.72(\text{TMA})_2\text{O}:0.0094 \text{Na}_2\text{O}:0.29 \text{Al}_2\text{O}_3:1 \text{SiO}_2:108.82 \text{H}_2\text{O}$ ) was aged for 3 days at ambient temperature. The crystallization was performed at 100 °C for 6 days. The solid product was recovered by centrifugation (20,000 rpm for 1 h), washed several times with distilled water, dried over night at 80 °C, and calcined in air at 550 °C for 8 h.

### 2.3 Preparation of samples

The waste lubricant oil samples were treated with 3 % sodium hydroxide solutions and then washed with water before pyrolysis. The catalysts were treated with 10 % sodium hydroxide solutions before using. Zeolites Na-Y were dehydrated at 150 °C for 3 h before added into the waste lubricating oil samples, 5 wt. % (Tan et al. 2014). To obtain an homogeneous dispersion the waste lubricant oil and zeolites were ultrasonicated for 1 h.

### 2.4 Pyrolysis process of waste oil

The experiments of the pyrolysis of the waste lubricant oil were performed in a laboratory scale apparatus. The main element of this device was a vertical cylindrical reactor of stainless steel, 127.0 mm height, 17.0 mm inner diameter, and 25.0 mm outer diameter, inserted vertically into an electrically heated tubular furnace. Heat to the vertical cylindrical reactor was supplied from an external heater, and the power was adjusted to give an appropriate heat-up time. A thermocouple was placed directly in the pyrolysis medium. The heater was started at 25 °C and terminated at the desired temperature of 700 °C. The pyrolysis products were collected within three different groups: as condensable liquid products, non-condensable gaseous products and solid residue.

### 2.5 Materials characterization

The characterization of materials was obtained by the combined use of different techniques. TEM images were obtained with a FEI Tecnai electron microscope operating at 200 kV with a LaB6 filament as the source of electrons. The preparation of samples for TEM analysis involved sonication in ethanol for 2–5 min and deposition on a carbon grid. XRD measurements were performed with a Bruker D8 X-ray diffractometer using  $\text{CuK}\alpha$  radiation. Powder samples were outgassed in He flow at 523K for 12h before measurements. FT-IR spectra were acquired by a Vertex 70 Apparatus (Bruker Corporation). Surface area and porosity characterization was obtained by  $\text{N}_2$  adsorption–desorption at 77 K with a Kelvin 1042 V3.12, COSTECH Instruments. Powder samples were outgassed in He flow at 300 °C for 1 h before measurements. The permanent gases were determined using a gas chromatography–mass spectrometry (GC-MS) (Thermo Fischer Scientific) by using HP-5 capillary column ( $0.25\mu\text{m}\sim 0.25\text{mm}\times 30\text{m}$ ). Temperature setting was as follows: injection port: 100 °C, column: 100 °C, detector: 120 °C. The chromatogram was calibrated with gases at known concentrations as standard mixtures. Helium was used as the carrier gas.

## 3. Results and discussion

The morphological and internal structural of zeolite Na-Y were determined by TEM analysis. The TEM images of the zeolite Na-Y at increasing magnifications are shown in Figure 1. The clear boundary shapes of the zeolite are very obvious. The size of the particles was between 40 and 50 nm.

The diffraction peaks of zeolite Na-Y are shown in Figure 1 top right side. The zeolite Y peaks can be observed in the XRD pattern at Bragg's angles  $2\theta = 6^\circ$  (1 1 1),  $10^\circ$ ,  $12^\circ$ ,  $16^\circ$  (3 3 1),  $19^\circ$  (3 3 3),  $20^\circ$  (4 4 0),  $24^\circ$  (5 3 3),  $27^\circ$  (6 4 2),  $31^\circ$  (6 6 0), and  $32^\circ$  (5 5 5), (Hriljac et al., 1993). As shown in the Figure, the sample appears crystalline. In particular, it can be noticed that the zeolite Na-Y are oriented by virtue of the large intensity of the (1 1 1) reflection  $2\theta = 6^\circ$  indicating the priority orientation of the (1 1 1) faces.

The FTIR spectrum, in the region of 400–1780  $\text{cm}^{-1}$  to characterize the framework vibrations of zeolites is shown in Figure 1 bottom right side. The band at 1640  $\text{cm}^{-1}$  belongs to the scissor vibration arising from the proton vibration in the water molecule. The bands at 1050 and 706  $\text{cm}^{-1}$  represent the asymmetric and symmetric stretching vibrations corresponding to the inner  $\text{TO}_4$  structure ( $T = \text{Si}, \text{Al}$ ), respectively, whereas the bands at 1170 and 788  $\text{cm}^{-1}$  represent the asymmetric and symmetric stretching vibrations corresponding to the external  $\text{TO}_4$  structure ( $T = \text{Si}, \text{Al}$ ), respectively. The band at 576  $\text{cm}^{-1}$  is attributed to the double ring external linkage peak associated with the FAU structure (Huang et al. 2010). The band at 460  $\text{cm}^{-1}$  is assigned to the structure insensitive T–O bending modes to the tetrahedral  $\text{TO}_4$  structure ( $T = \text{Si}, \text{Al}$ ).

The  $\text{N}_2$  adsorption–desorption isotherms and pore distribution of the zeolite Na-Y nanocrystals are given in Figure 2. The fast uptake at very low relative pressures corresponds to the filling of the micropores (see Figure 2a). The hysteresis curve, that starts at  $P/P_0$  of about 0.6, matches with type IV isotherm. The mesopores, generated by the secondary arrangement in the crystals, are responsible for the hysteresis. The sample exhibited a BET surface high area of 602  $\text{m}^2/\text{g}$  (Nguyen et al., 2016). A micropore volume of 0.15  $\text{cm}^3/\text{g}$  was determined by the t-plot. The mesopore volume of the samples was estimated to be 0.18  $\text{cm}^3/\text{g}$  (BJH method). The sample contains both micropores and mesopores with pore size of 0.68 nm and 3.54 nm, respectively.

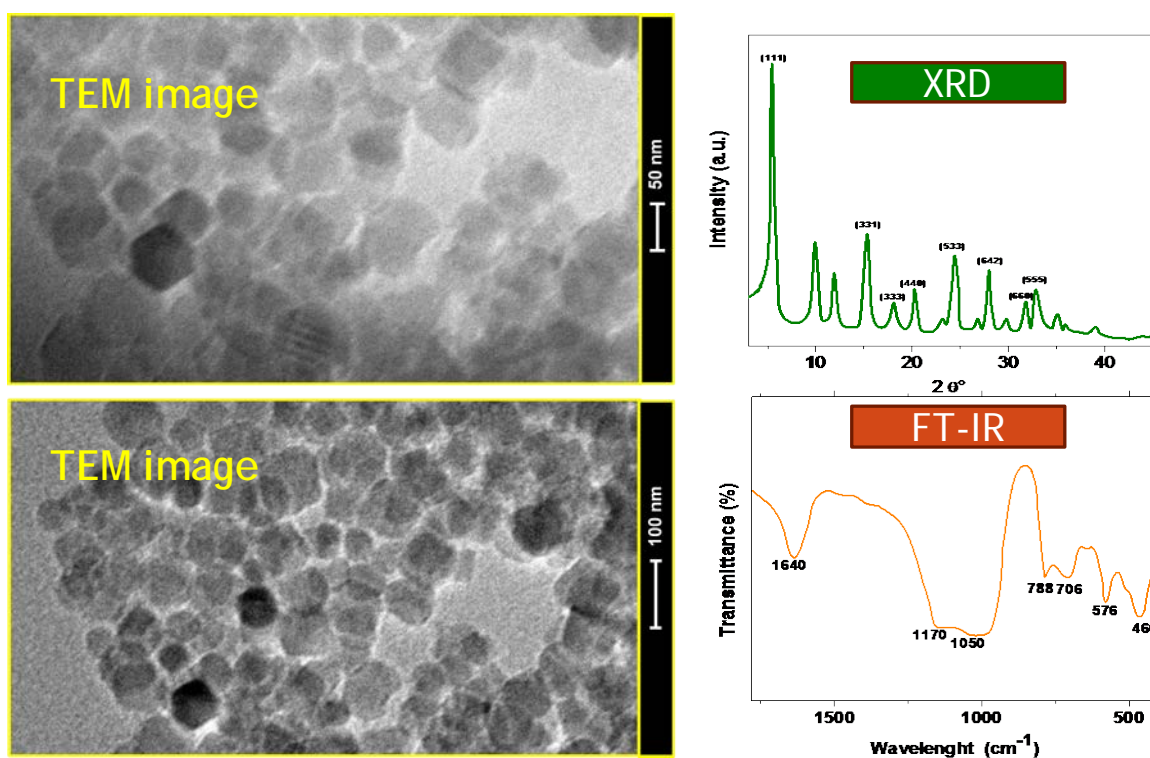


Figure 1: Tem images of zeolite Na-Y at different magnifications. XRD spectrum of zeolite Na-Y. FTIR spectrum of zeolite Na-Y.

### 3.1 Catalytic effects on gas evolving

The incondensable gases produced from pyrolysis consist mainly of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{CO}_2$ .

In particular, the catalytic effects of zeolite Na-Y on gases evolving during pyrolysis of waste lubricant oil is described below. Table 1 and Table 2 show the concentration values (% mol/mol) of the gases at different sampling time (S.T.). Specifically, in the presence of Na-Y zeolite, the concentrations of  $\text{CH}_4$  and  $\text{CO}_2$  decrease with time, meanwhile the  $\text{H}_2$  yield increases. The concentration of  $\text{H}_2$ , in the presence of zeolite, reaches the maximum value after 16 minutes from the beginning of the process.

In particular, the average concentration of  $\text{H}_2$  produced during catalytic pyrolysis increases with respect to untreated (without zeolite), i.e. our zeolite Na-Y catalyst favors  $\text{H}_2$  formation. Finally, the average yield of each gas species is shown in Table 3. It is interesting to note that the total yield of all gas species is increased in presence of the Na-Y zeolite catalyst.

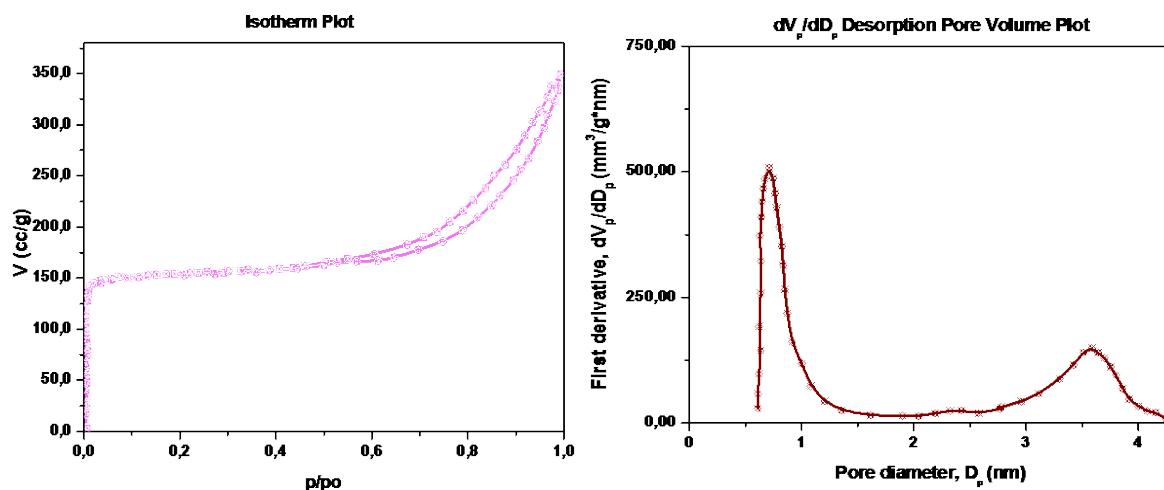


Figure 2:  $N_2$  adsorption-desorption isotherm, and BJH pore size distribution, of zeolite Na-Y.

Table 1: Concentration of gases evolved during different period (% mol/mol).

S.T. (min)	8.00				16.00				24.00			
	$H_2$	$CH_4$	CO	$CO_2$	$H_2$	$CH_4$	CO	$CO_2$	$H_2$	$CH_4$	CO	$CO_2$
Untreated	0.0162	0.000	1.3104	1.9935	1.5834	1.2849	3.1612	2.5799	4.5623	1.4116	3.0742	1.3581
Zeolite Na-Y	0.0081	0.000	0.2242	0.5785	16.080	0.6893	2.1986	2.1093	7.4339	0.9007	2.9017	1.1154

Table 2: Concentration of gases evolved during different period (% mol/mol) and average concentration.

S.T. (min)	32.00				40.00				Average Concentration (%)			
	$H_2$	$CH_4$	CO	$CO_2$	$H_2$	$CH_4$	CO	$CO_2$	$H_2$	$CH_4$	CO	$CO_2$
Untreated	5.0861	1.5837	3.5840	4.7571	2.9082	1.1211	2.2039	1.9541	2.8312	1.0803	2.6667	2.5285
Zeolite Na-Y	2.9578	0.5314	2.0783	0.7282	1.5740	0.4004	1.4852	0.7481	5.6108	0.5044	1.7780	1.0559

Table 3: Estimated yield of each gas species evolved during pyrolysis of waste lubricating oil with and without Na-Y zeolite (wt%).

	$H_2$ yields	$CH_4$ yields	CO yields	$CO_2$ yields	Total Gas Yields
Untreated	1.6	5.0	21.5	21.0	60.1
Zeolite Na-Y	4.7	2.5	25.8	32.0	65.0

#### 4. Conclusions

Pyrolysis is able to reduce a bulky, high-polluting industrial waste, to give energy and/or valuable chemical compounds. This technology not only provides a route to recover potentially useful products from environmentally hazardous waste oils, but it also serves as an effective disposal method for the waste oils. In particular, the ability of Na-Y zeolite to improve  $H_2$  production, during pyrolysis of exhausted lubricating oils, has been successfully demonstrated. These results contribute to choose pyrolysis for “in loco” production of high added value gas from waste oils.

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