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PYROLYSIS OF WASTE GREENHOUSE POLYETHYLENE TO PRODUCE POLYETHYLENE WAX

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Necdet Serkan BAYIR tarafından Yüksek Lisans tezi olarak sunulan **“Pyrolysis Of Waste Greenhouse Polyethylene To Produce Polyethylene Wax”** başlıklı bu çalışma, E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 06.09.2010 tarihinde yapılan tez savunması sınavında aday oy birliği/oy çokluğu ile başarılı bulunmuştur.

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ÖZET

ATIK SERA POLİETİLENİN PİROLİZİ İLE POLİETİLEN VAKSLARININ ÜRETİMİ

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Katı atıkların içindeki plastik maddelerin büyük bir kısmını poliolefinler oluşturmaktadır. Bu poliolefinlerin geri dönüşümlerine örnek olarak yüksek yoğunluklu polietilen şişelerin geri dönüşümü, motor yağı kutularının geri dönüşümü, alçak yoğunluklu polietilenin geri dönüşümü ve propilen gibi diğer poliolefinlerin geri dönüşümünden bahsedilebilir. Bu proje genel olarak polietilenin geri dönüşümü üzerine hazırlanmıştır. Bir termoplastik olan polietilen ilk olarak 1940 yılında bulunmuştur. Alçak yoğunluklu, lineer alçak yoğunluklu ve yüksek yoğunluklu polietilen olmak üzere üç çeşit polietilen vardır.

Bu çalışmada polietilen (PE) filmleri azot atmosferinde ısısal bozunmaya uğratılarak vaks niteliğinde ürünler elde edilmeye çalışılmıştır. Polietilenin ısısal bozunması gelişigüzel zincir bölünmesi mekanizması ile yürümekte, polimerleşme derecesinin değişimi ile zincir bölünmelerinin sayısı ölçülmekle birinci dereceden kinetik davranış göstermektedir. Burada önemli nokta bozunma sıcaklığı uçucu ürünlerin büyüklüklerini belirlediğidir. Sıcaklık arttıkça gazlaşabilen parçacıkların minimum uzunlukları azalmaktadır. Piroliz, hurda lastiklerin ısısal destilasyonu ile karbon siyahı ve piroliz yağına dönüştürülmesi amacıyla çalışılmıştır.

Deneysel çalışmalar Ege bölgesinde yaygın olarak kullanılmakta olan PE filmlerine yoğunlaşılmıştır. Optimum sıcaklık en yüksek vaks verimi % 84 ve ürün kalitesi esas alınarak 5 dakikada 440 ^{0}C olarak bulunmuştur. Donma ve damla erime sıcaklıkları, piroliz işleminin optimizasyonu için kullanılmışlardır.

Hammadde ve ürünlerin tanımlanmaları için ilaveten FTIR ve DSC cihazları kullanılmıştır.

Sonuç olarak laboratuar düzeyinde yapılan çalışmalar ümit verici bulunmuş olup özellikle piroliz ve soğutma kısımları birbirine bağlı reaktör tasarımı için daha ileri çalışma yapılması gerekmektedir. Gaz haldeki ürünlerin yoğuşması ile elde edilebilecek ürünlerin, fırının ısıtılmasında yakıt olarak kullanılabilmesi düşünülmektedir.

Anahtar Sözcükler: Alçak Yoğunluklu Polietilen, Piroliz, Geri Dönüşüm, Atık Sera Polietilen filmi

ABSTRACT

PYROLYSIS OF WASTE GREENHOUSE POLYETHYLENE TO PRODUCE POLYETHYLENE WAX

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Polyolefins represent the largest plastics constituent in the municipal waste stream. Recycling of these polyolefins have various types such as HDPE bottle recycling, recycling of HDPE motor oil containers, recycling of HDPE automotive fuel tanks or LDPE recycling and LLDPE recycling and recycling of other polyolefins like polypropylene etc. But in this report mostly recycling of polyethylene is discussed. Polyethylene, a thermoplastic, was first discovered in 1940's. There are three types of polyethylene, low density, linear low density and high density polyethylene.

In this study polyethylene(PE) films are subjected to thermal degradation to obtain waxy products under nitrogen atmosphere. Thermal degradation of PE has been described as occurring by random chain scission mechanism and it obeys first order kinetics when the number of chain scission is measured by the change in the degree of polymerization. Degradation temperature and time influence inversely the size of the products which are gaseous, liquids and solids.

Experimental studies have been focused on scrap greenhouse PE films which are extensively used in Aegean area. Optimum temperature for pyrolysis under nitrogen atmosphere was found as 440 ^{0}C and 5 minutes for the highest wax yield which was 84 % and the quality of the product is measured by using standard techniques.

Congealing and drop melting temperatures were measured for the optimization of the pyrolysis process. FTIR and DSC were also used to identify the raw materials and the products.

Bench scale experiments gave satisfactory results in obtaining waxy products from waste greenhouse polyethylene which could not find any other application in our country. It is thought that gaseous products could be collected and they can be used as fuel gas for pyrolysis oven.

Key Words: Low Density Polyethylene, Pyrolysis, Recycling, Greenhouse Films

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ABBREVIATIONS

DOE : Department of Energy
ECUT : Energy Conservation and Utilization Technologies
BTX : The pyrolytic oil contains high levels of aromatic hydrocarbons-
benzene, toluene and xylene
PE : Polyethylene
PP : Polypropylene
ABS : Acrylonitrile-butadiene-styrene
PS : Polystyrene
HDPE : High-density polyethylene
LDPE : Low-density polyethylene
PVC : Polyvinyl chloride
PET : Polyethylene terephthalate
Py-GC : Pyrolysis-Gas Chromotography

α : degree of conversion or fractional conversion of the reaction
R : Gas constant
T : Absolute Temperature
dXi/dt : formation rate of i reactant (s−1)
E_a : activation energy (kJ mol−1)
k_0 : frequency factor
k_{AC} : kinetic constant for the formation of char from aromatics
k_{PG} : kinetic constant for the formation of gas from the plastic (s−1)
k_{PL} : kinetic constant for the formation of liquid from the plastic (s−1)
k_{PW} : kinetic constant for the formation of waxes from the plastic (s−1)
k_{WA} : kinetic constant for the formation of aromatics from waxes
k_{WL} : kinetic constant for the formation of liquid from waxes
$\dot{m}_i$: mass flow rate of each i component (kg s−1)
M_0 : total mass of plastic in the feed (kg)
M_i : mass of lump i formed up to a given time (kg)
n_l : number of lumps of each scheme
n_T : number of temperature values

1.0 INTRODUCTION

The amount of plastic materials used in different technologies is continuously increasing. Plastic materials are used for greenhouse covers, mulching, piping, packaging and other applications. Films used for greenhouses can be considered as an easy source of materials for recycling. Indeed, large amounts of film can be easily collected and because of the homogeneity of the polymers used for this application, the recycling operations can be relatively easy. The secondary materials are usually employed for the production of blown film for packaging.

However the polymer materials used for these films is changing and in particular the use of blends is continuously increasing like the use of additives. These additives are used in relatively large amounts for different aims, like photooxidation resistance, antifog, etc. Moreover, the films can absorb fertilizers and pesticides that can compromise the use of secondary materials coming from greenhouse cover films in many applications (Dintcheva et al., 2001).

Consumption of plastics has increased dramatically over the last 50 years. In 1940, the consumption of plastics was around 0.04 million tons; in 1962, the consumption increased to around 1 million tons per year; for 1992, it was 86 million tons; and for 2002, it was assumed to be approximately 110 million tons in the world. Plastic wastes constituted 18 million tons of the 2.8 billion tons of total wastes in Western Europe for 1996. The consumption of plastics has been increasing rapidly which will no doubt put pressure on crude oil and natural gas usage for production of plastics, since the world deposits are declining. In the USA, among the types of plastic packaging material, polypropylene (PP) ranked fourth after Low Density (LD) and High Density (HD) polyethylene (PE) and polystyrene (PS). The consumption figures indicate that waste plastics are always a potential environmental hazard and a great burden on resources (Kıran et al., 2004).

Since 1970, these plastic wastes were either burned or buried underground. The conventional solution of land filling is no longer an acceptable means for disposal of plastic due to serious environmental concerns. Plastic waste recycling can be categorized into four modes. Primary recycling deals with conversion into products similar in nature to the original product. Secondary recycling involves conversion into products of different forms for less demanding applications. Tertiary recycling converts wastes into basic chemicals or feedstock. Quaternary recycling retrieves energy from wastes through combustion. Of the possible technologies for the conversion of waste to useful products, on that has attracted some study and development effort is pyrolysis (Hanoğlu, 1992).

There still exists the necessity for the development of an appropriate plastic waste management policy. One of the desired methods of plastic waste management is the reuse of products in their original structure. However, this is possible for some wastes and there is also an obvious limit on the number of cycles for each material. The recycling of material, the incineration with and without heat recovery and the use of landfills are among many ways of processing waste plastics. Pyrolysis is one of the well-known processes for the chemical and resource recycling of plastics.

Pyrolysis for the simultaneous generation of oils and gases can be convenient to obtain hydrocarbons and even to recover crude petrochemicals or to generate energy from waste plastics (Kıran et al., 2000).

The output products from the degradation of the plastics by the application of heat under oxygendeficient conditions can be used in petrochemical and chemical industries or they can be combusted and used for heating. Pyrolysis processes are generally classified into low, medium and high temperatures based on the range of temperatures used to destroy the plastic structure. The products obtained from pyrolysis of plastics depend on the type of plastics, feeding arrangement, residence time, temperatures employed, reactor type and condensation arrangement. Low temperature processes generally enhance liquid products and high temperature processes enhance gaseous products.

A comparison of waste and virgin polypropylene (PP) plastics under slow pyrolysis conditions is presented. Moreover, mixtures of waste PP with wastes of polyethylene (PE) and polystyrene (PS) were pyrolyzed under the same operating conditions.Not only the impact of waste on degradation products but also impacts of the variations in the mixing ratio were investigated.The thermogravimetric weight loss curves and their derivatives of virgin and waste PP showed differences due to the impurities which are dirt and food residues.The liquid yield distribution concerning the aliphatic, mono-aromatic and poly-aromatic compounds varies as the ratio of PP waste increases in the waste plastic mixtures.In addition to this, the alkene/alkane ratio of gas products shows variations depending on the mixing ratio of wastes (Kıran et al., 2004).

Nickel and rate earth metal exchanged Y-type zeolite catalyst (Ni-REY) was prepared for producing light fuels (gasoline and kerosene) by the catalytic cracking of heavy oil from waste plastics in a steam atmosphere. The Ni in the catalyst was found to exhibit catalysis for transportation of hydrogen atoms from steam to hydrocarbons. In a steam atmosphere, strong acid sites of the catalyst, which usually cause excessive cracking, were covered with steam molecules, leading to a high yield of liquid fuels. Experiments using MFI zeolite in a nitrogen atmosphere were also conducted for comparison. During the repetition of sequences of reaction and regeneration of the catalysts, MFI zeolite was gradually deactivated, whereas Ni-REY was found to show constant activity. Furthermore, the selectivity towards gasoline was higher than MFI zeolite (Ni-REY in steam: 78%, MFI type zeolite in N_2:35%) (Masuda et al., 1999).

The effect of the degree of crosslinking on pyrolysis was examined. Catalyst activity was also found to be effected by changing crosslinking density (Marcilla et al., 2006).

Wax is a collective term for a range of natural or synthetically derived substances used in a wide variety of applications; among the foremost in importance are candles, packaging, rubber, plastics, polishes, anti corrosives, cosmetics, inks and paints.

Wax is a generic term for a range of natural or synthetic products. For convenience the range can be subdivided:

- Natural waxes
- Synthetic waxes
- Mineral hydrocarbon waxes
- Petroleum waxes

Waxes are usually defined by their characteristic properties (see also International Customs Tariff, Harmonized System HS 3404):

- solid at 20° C, varying in consistency from soft and plastic to brittle and hard
- as solids as coarse to finely crystalline, transparent to opaque, but not glass-like
- have relatively low viscosity slightly above the melting point
- melt above 40° C without decomposition
- consistency and solubility are highly temperature dependant
- buffable under slight pressure
- burn with yellow flame can form pastes or gels when dispersed in solvents
- exhibit low thermal and electrical conductivity

Types of waxes can be listed as;

Natural (non fossil) Waxes

The natural wax can be of vegetable or animal origin. The predominant wax of animal origin is beeswax (E 901). The most important representatives of vegetable origin are:

- carnaœba (E 903)
- candelilla (E 902)

Mineral Hydrocarbon Waxes

- Montan Wax - derived by solvent extraction of lignite
- Ozo Kerite

Petroleum Waxes

Petroleum waxes are hydrocarbons derived from petroleum. There are four main types:

- slack wax - unextracted wax derived from dewaxing base distillate lub oil streams
- paraffin - deoiled slack wax consisting predominantly of straight chain alkanes
- microcrystalline (E 905) - branched and cyclic alkanes from deoiling residual bright stock lube oil stream
- petrolatum - bright stock deoiled residual lube oil or blends of oils and waxes - petroleum jellies

Synthetic Waxes

- Polyolefin waxes
- Fischer-Tropsch wax

In Europe the interests of all wax producers have been represented by the European Wax Federation since 1979. More detailed knowledge can be found from the web adress of http://www.wax.org

1.1 The History of Petrochemical Industry in Turkey

The petrochemical industry uses petroleum and natural gas based feedstocks such as naphtha, LPG, gas oil to produce plastics, rubber and fiber raw materials and other intermediates which are consumed by several sectors such as packaging, electronics, automotive, construction, textile and agriculture.

The petrochemical industry has started to develop in the second half of the 20th century and has become one of the foundation stones of the modern economy in the last fifty years due to its extremely wide product range and application field. Thousand of petrochemical products utilized by consumers, became an indispensable part of human life and the developments in the petrochemical industry raised the living standard significantly.

The current market value of the petrochemical industry is about 500 billion dollars. This value equates to about 8% of world trade and about 30% of the total chemical market.

The petrochemical industry experiences cycles in prices and profitability parallel to the developments in the world economy and in conjunction with the movements in supply and demand. In these cycles, high profitable periods of 3-4 years followed by low profitable or unprofitable periods of 4-5 years.

In the world petrochemical sector, the low profitable period starting with the Asian crisis at the end of 1997 has been continuing. A new profitable period, which will start with a fundamental recovery in 2004 and will peak in 2005, is expected in the sector.

In recent years, structural changes are being carried out in the petrochemical industry. The companies try to increase their competitive positions and profit margins by means of narrowing, broadening or changing their fields of activities either individually or by merging with other companies.

Petrochemical industry is open to global competition and raw material, market and technological advantages play significant roles in this competition. For the new investments, certain regions having feedstock advantages and large/rapidly growing markets are being preferred by the petrochemical companies. In the next years, most of the new investments will be realized in the Middle East and Asia (particularly in China).

Olefins are the building blocks of many petrochemicals. The developments in the olefin markets reflect the general performance of the petrochemical industry.

Ethylene is the most important olefin and the largest produced basic petrochemical. The world ethylene demand is anticipated to reach from 98 million tons in 2003 to 116 million tons in 2010. Average annual growth rate of 4-4.5% is estimated for ethylene by 2010, and it is necessary to add over the period 4-5 million tons of new ethylene capacity per year just to keep up with growth.

The petrochemical industry that entered to Turkey in 1960’s has demonstrated a great development within a very short time. Petkim was established in 1965 to start and develop a petrochemical industry in the country.

The first petrochemical complex of Petkim was established at Yarımca and started up in 1970. Due to the rapidly growing domestic demand, Yarımca Complex had started to become insufficient to meet the increasing demand although the production capacities of most of the plants that exist in Yarımca Complex were expanded by 100 %. The second complex of Petkim was established at Aliağa by using optimum capacities and modern technologies of those days and started up in 1985.

Most of the plants in Yarımca Complex were closed in the period 1993-1995 because they had completed their economic lives and had lost their competitiveness. Petkim transferred Yarımca Complex with its 5 plants (SBR, CBR, CB, BDX, PS) in operating position to TÜPRAŞ Turkish Petroleum Refineries Corporation on November 1, 2001.

Petkim, as the sole producer of basic petrochemicals and the biggest producer of thermoplastics and intermediates, is the leader company of Turkish petrochemical industry. Apart from Petkim, the other petrochemical companies in Turkey are SASA (240 000 tons/year DMT), TÜPRAŞ (33 000 tons/year SBR, 20 000 tons/year CBR, 40 000 tons/year CB,33 000 tons/year BDX,27 000 tons/year PS) and Başer Petrokimya (40 000 tons/year PS).

The demand for petrochemical products in Turkey has been increasing faster than that of the developed countries and world average level. On the other hand, domestic supply does not increase at the same rate. In order to meet the rapidly growing demand, Petkim realizes expansion and modernization investments that increase its capacities significantly. However, these capacity increases are very insufficient to meet the rapidly growing domestic demand. The share of the domestic production in consumption has been decreasing rapidly, and the import of petrochemical products of Turkey has also been increasing rapidly. Petkim was able to meet only 30% of domestic petrochemicals demand in 2003. This situation negatively affects the competitive strength of Turkish petrochemical industry and causes the high added value of petrochemicals to remain abroad.

Turkish petrochemicals market is not saturated yet. While thermoplastics consumption in Turkey is around 29 kg per capita, this rate varies between 75-100 kg per capita in developed countries.

It is seen that Turkish petrochemical industry has a big potential for growth, having considered the factors such as the level of industrialization in Turkey, rapid population growth and developments in various industrial sectors.

The most significant advantage of Turkish petrochemical industry, despite the close proximity of feedstock rich countries with big petrochemical producers, is the level of domestic demand, which allows the establishment of production facilities in world scale capacities.

Because of these reasons, necessary investments for Turkish petrochemical industry should be realized immediately (Petkim, http://www.petkim.com.tr), (Date of Access: May 4th, 2010).

1.2 Recycling and Recovery of Plastic Wastes

European packaging disposal laws are beginning to expose the inadequacy of material recycling systems for handling mixed post-consumer plastics waste. Converting polymers back into short-chain chemicals for reuse in polymerization or other petrochemical processes –chemical recycling-is becoming feasible. The advantage of the chemical recycling process is that chemicals produced are just as good as the originals, while material recycling always produces some degradation in the resins used (Mapleston, 1993).

The need for new solutions for problems of solid waste disposal has been apparent since the late nineteen seventies and early nineteen eighties with the ever-increasing pace of plastics volumes produced, utilized for new applications and discarded. The issues of environmental contamination and of energy conservation are now driving forces for the development of new generations of recoverable polymers and of creative new technologies for utilization of polymeric materials post use.

Due to the recycling of municipal waste results very few percent of polyethylene can be recycled in 2007 in United States. It is seen in Figure 1.1

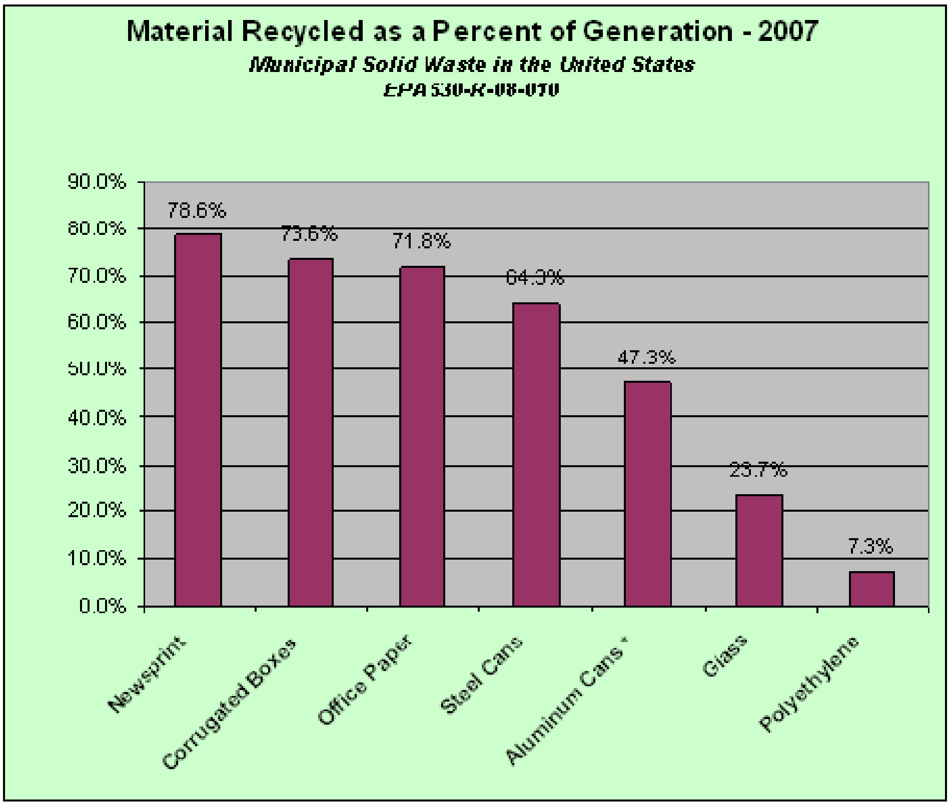


Figure 1.1 Material Recycled as a percent of generation in 2007

In 1980, the Department of Energy (DOE) established the Energy Conservation and Utlization Technologies (ECUT) program with the mission to conduct generic, long-term high-risk applied research and exploratory development in areas pertaining to energy conservation. In the ECUT materials program, research on polymer recycling and recovery was an important element. For synthetic polymers, the initial focus was on technology for producing commercially viable commodities from automobile shredder residue (Plastic Institute of America (PIA), 1987).

Longer range efforts were contemplated on developing novel separation techniques, on recovery of value from specific polymer classes and on fundamental investigations of approaches to utilization and reuse of advanced polymeric materials and composites. The DOE/ECUT policy and program have been perhaps the most important factors in determining the progress of the nineteen eighties in polymer recycling research and development. The evaluation of current status and future needs can be attempted only in the context of accomplishments directly or indirectly related to this element of the DOE program.

The U.S. EPA calculated that 150 thousand tons of LDPE/LLDPE bags, sacks, and wraps were recovered in 2003, for a recycling rate of 5.7 percent. The overall recycling rate for LDPE in MSW was 2.4 percent. The overall recycling rate for LDPE and LLDPE in Australia was reported to be 12.2 percent in 2003 above the 2002 rate of 11.2 percent but lower than the 2001 rate of 13.4 percent. (Recycling of Low-Density Polyethylene (LDPE) And Linear Low-Density Polyethylene (LLDPE) by Charles A. Harper, http://www.globalspec.com) (Date of Access: September 02nd, 2010)

Figure 1.2 LDPE/LLDPE in municipal solid waste in the U.S. in 2003

The subjects of natural polymers, biodegradable polymers, renewable resources and rubber require consideration of factors that do not necessarily apply to recycling of synthetic polymers and are beyond the scope of the discussion which follows (Tesoro and Wu, 1994).

1.2.1 Methods for Recycling Plastics

Films for greenhouses are an attractive source of post-consumer plastic materials because they are mainly made of polyethylene and can be easily collected in large amounts in small zones. The types of polymers for this application are however increasing and the films contain not only additives and stabilizers but also fertilizer and pesticide residues. Finally the extent of photo oxidative degradation undergone during the use can strongly influence the recycling operations and the final properties of the secondary material. In this work, a complete characterization of post-consumer films for greenhouses has been carried out and the properties of the recycled material have been correlated with the number of reprocessing steps and compared with those obtained by reprocessing virgin scraps of the same composition. The presence of small amounts of low molecular weight compounds does not compromise the use of the recycled plastic in many applications. The mechanical properties decrease with the number of reprocessing steps and with increasing level of photooxidative degradation but are good enough for many applications.

Pyrolysis of plastics is well-known as an analytical procedure and is also a potential method for recycling polymers. Unlike thermolysis in dilute solution, where solubilized polymers undergo chain scission to products that mostly remain in the constant-volume liquid phase, pyrolysis usually refers to a melted plastic thermally depolymerizing to lower molecular-weight (MW) compounds that vaporize and reduce the melt volume. The vaporization process makes pyrolysis kinetics more complex and difficult to characterize quantitatively than solution-phase thermolysis. It is showed that combining kinetic theory and vapor-pressure thermodynamics yields activation energies for vaporization on the order 18-50 kcal/mol for alkanes of chain length 19-94. Because chain-scission activation energies are also in this range, determining the rate-controlling process may not be straightforward.

A recent review of low-temperature pyrolysis (T<450°C) states that most chemical-reaction kinetics studies of pyrolysis were performed by standard thermogravimetric analysis (TGA). Weight-loss data for a small polymer mass (a several milligram sample) of polymer in a small heated crucible comprise the primary information for determining pyrolysis kinetics. The review, in a critical discussion of several models for analyzing TGA data, pointed out that the observed weight loss in pyrolysis involves evaporation of low-MW products. Any low-MW molecules initially in the polymer will also evaporate. The empirical power-law rate expression employed in most studies to fit TGA weightloss data is considered valid only at large polymer conversions, where random scission of the remaining lower-MW polymer molecules yields products that can vaporize. The widespread use of the simple power-law model is a probable reason that reported rate coefficients differ by a factor of 10. Reported kinetic parameters (preexponential factor and activation energy) for polyethylene also cover a wide range. Westerhout et al. (1998) proposed a random-chain-dissociation (RCD) model, based on evaporation of depolymerization products less than a certain chain length. For the screen-heated pyrolysis system, as well as for thermogravimetry, mass transfer of vaporized depolymerization products can strongly influence rate measurements. Such interphase mass transfer depends on a driving force that should account for equilibrium at the vapor-liquid (melt) interface. Evaluation of a flow reactor with entrained polymer particles showed that melted particles tended to stick to the reactor walls, making their residence times unpredictable (Naime et al., 1998).

Pyrolysis of plastics such as polyethylene (PE) and polypropylene (PP) of olefin series to gaseous products, the catalysts with high cracking property are needed.

Catalytic and thermal cracking of polyethylene waste were investigated in continued tube reactor system. HZSM-5 and equilibrium FCC type catalysts were tested. Both the resistance to deactivation and the regeneration process of the catalyst were studied. Reaction temperature of 545°C and residence time of 20 min were used during the cracking treatment. The reaction products were analyzed and the textural properties of catalysts were also determined. It was found that after the first reaction run the FCC catalyst lost 75% of its cracking activity, in case of HZSM-5 the rate of deactivationwas higher. The cracking activity of catalyst could be improved by regeneration process with only 2–3% compared to the coked catalyst. The isomerisation effect of the catalysts was also observed. The effect of coked FCC catalyst could be improved by the regeneration process with 50% in case of HZSM-5 it was only 25% (Angyal et al., 2009).

Polyethylene is the most used and available plastic packaging material and it has been widely studied for its thermal degradation. Its combustion produces many gaseous compounds, the nature of which depends on the conditions used such as temperature and oxygen availability. Moreover, the energy consumption during the pyrolysis process might be high, increasing the operating costs. More and more, the catalysed pyrolysis of plastics is being considered as a means to reduce these costs. Polyaromatics and their derived-compounds are among the species for which emissions must be particularly controlled. Studies on the degradation of polyethylene to aromatic hydrocarbons on metal-supported activated carbon catalysts, the effects of adding metals, or the effect of iron loaded activated carbon fluidized bed have been investigated to control the degree of aromatization of pyrolysis products. Similarly, the influence of metals on the thermal treatment of metal/plastics mixtures has been studied to control aromatic emissions, char formation, or in the search for appropriate flame retardants.

Iron and copper chlorides are frequently suspected of the catalytic formation of hazardous unwanted compounds. The presence of iron and copper has been demonstrated to drastically influence the thermal decomposition of polyethylene. Thermal decomposition processes of polymers were shown to be modified by the catalytic action of iron and copper chlorides. Many studies available on the effect of transition metal elements on the pyrolysis of various plastic materials. However, we envisioned that it is worthwhile to reinvestigate the fundamental pyrolysis processes of organic polymers on a continuous pyrolysis temperature scale (Lei, 2006).

Other plastics including acrylonitrile-butadiene-styrene(ABS) and polystyrene(PS) can be easily pyrolyzed under the lower temperature than PE and PP without catalysts for the production of light oil.

The consumption rates of plastics go up rapidly and their quantities reach to three million tons per year in 1996. The order of production quantity of waste plastics is PP> HDPE> LDPE>PVC> PS>ABS. In these plastics, PVC is mostly in the industrial use and is rarely produced from municipal wastes.

Profiles extruded from recycled HDPE are finding increased use in such applications as decking, fence posts, road posts, railroad sleepers and similar areas replacing wood and concrete. For instance, plastic lumber is approximately four times more flexible than wood. Diverse applications such as marine structures, highway barricades, roadside reflector posts, drainage troughs for runoff from barns, antifreeze bottles, recycling collection containers as well as various large blow moldings have all been developed and commercialized for recycled HDPE.

An important problem in recycling is contaminations. Contamination in HDPE can arise from a number of sources. Potential problems can occur at various stages of the products life cycle: during fabrication, during use, during collection by the environment and by reprocessing. Types of contaminations can be listed as polypropylene contamination, copolymer HDPE contamination in homopolymer HDPE, PET contamination, adhesive contamination, paper contamination, contamination by packaging contents and additives and contamination by reprocessing.

PP contamination in HDPE arises from both injection molded PP closures and caps as well as from PP bottles which are mistaken for HDPE bottles. Recycled HDPE homopolymer can also be contaminated with HDPE copolymers such as ethylene-butane copolymers used in the manufacture of detergent. Because of its widespread use for carbonated beverage bottles, PET is often a contaminant in PE at the collection and sorting stage. Hot melts can be particularly problematic during the recycling of HDPE. Many HDPE and PET bottles have paper labels which are usually removed during the washing stage of the recycling process. HDPE bottles are often contaminated by their contents that have migrated into the polymer or by residues which are difficult to remove by standard cleaning methods. Pigment contamination is a major problem in HDPE recycling in that it leads to a highly variable and generally dark colored recyclate. Recycling of HDPE PCR by melt extrusion can lead to crosslinking during the thermal reprocessing stage since the antioxidant added initially. Another common source of contamination in recycled HDPE is black specks. These are small areas of highly degraded polymer that have been carbonized due to excessive residence time in an extruder.

LDPE recycling is widespread although not to the magnitude as HDPE recycling. The majority of LDPE that is recycled originates from post industrial scrap and there is only a limited proportion of recycled LDPE which can be regarded as post consumer recyclate. A significant source of LDPE recyclate comes from pallet stretch wrap. Almost every distribution operation uses LDPE stretch wrap to stabilize loads on pallets. Garbage bags can be made from recycled LDPE at levels of 70-90 wt% the LDPE is generally sourced from post industrial pallet wrap.

There are contamination problems in LDPE as well. The contamination levels in mulch film make its recycling particularly challenging. Soil contamination can be as high as 30-40% and also it was found that vegetable matter coming from harvested plants could not be removed during the washing operation. Other contaminants are fumigants.

Another type of polyolefin recycling can be said as polypropylene recycling. The majority of recycled PP is recovered from automotive applications such as battery cases, car bumpers and dash boards. PP sacks, bottles strapping and industrial film scrap of biaxially oriented PP are other sources of recycled PP. Mostly automotive companies are investigating the recycling of PP. The main uses of recycled PP are automotive applications such as PP bumpers, splash shields, parts of air conditioner and air flow vents and valves, visors, instrument panels etc.

In order to determine the pyrolysis of PE to ethylene and other light hydrocarbons from a certain molecular weight range, pyrolysis of PE and PE wax was carried out by using Py-GC. The pyrolysis of PE wax has the same behavior as that of PE if both are pyrolyzed at the same temperature range. The pyrolysis of PE and PE wax are the same as that of heavy oil. The ethylene is produced at the beginning of the pyrolysis. At the same time, hydrocarbons of C_2-C_{40}, including parafin olefins and a, ω-dienes, were produced at the same time. The pyrolysis of PE and PE wax can be described by a first-order reaction model. This indicates that the traditional kinetics of the PE pyrolysis omitted the process of PE to PE wax. Actually, the whole pyrolysis process can be divided into 2 parts. At first, PE gradually decomposes into PE wax with a molecular weight range of 1,000 to 4,000. Second, PE wax decomposes into ethylene and other light hydrocarbons (Xing et al., 2003)

With a view to the environmental protection and reduction of non-regeneration resource, recycling technology for converting to oil from plastic wastes has drawn much attention in China. Some universities and institutes have developed the basis theories and the technology for industrialization of plastic liquefaction. Many pilot plants have been built up near Beijing, Nanjing, Xi'an, etc. But, some problems have appeared accordingly.

Firstly, there being no effective collecting system and transportation and sorting the collected waste plastics simply by manual, as a result, the collected plastic wastes cannot satisfy the continuous production on a large scale.

Secondly, the secondary pollution has not been seriously considered in the process of waste plastics. The environmental considerations deals with heat energy waste exhaust gas emission, water and dust waste, and the like.

Thirdly, there is no technological standard for the recycling of plastic wastes in China. The article explains upon the current situation of plastic wastes and their recycling technology for recovering to oil in China. As one of the most fast developing industries in China, the plastic industry maintains a growth rate of more than 10% per year (Guang et al., 2007).

There are six main plastics occurring in European municipal solid waste, high density polyethylene (HDPE); low density polyethylene (LDPE); Polypropylene (PP); polyvinyl chloride (PVC); polystyrene (PS) and polyethylene terephthalate (PET). However, the polyethylene plastics, HDPE and LDPE, make up over 40% of the total plastic content of municipal solid waste. Recovery increased to a total of 5.32 million tonnes, 30 wt.% of the total plastics waste stream, reducing the amount of plastics sent to landfill by 9 wt.%. Energy recovery of plastics waste has increased, with a rise of more than 20 wt.% by weight to 3.35 millions of tonnes. Research into alternative methods of recycling plastic waste is being carried out. Pyrolysis is an alternative process to incineration and material recycling. This approach of hydrocarbon processing has been investigated earlier but only recently interest in it has been increased. This method allows the recovery of the monomer and the production of other petrochemical products (Mastral and Esperanza, 2002).

Waste plastics can be reused as valuable resources according to the treatment technologies. The mechanical recycles for the production using the same material can be recommended as a desirable technology because this makes no more pollution problems. But it is very difficult to separate various waste plastics with dust and metals into one-component raw material which can be recycled without any problems. So, thermal recycle technologies are the objects of interest as alternatives for the mechanical recycle technologies.

In these technologies, pyrolysis may be favorably used for oil and monomer recovery from waste plastics. Also, this technology has more advantages than combustion technology in the view of discharging fewer pollutants. Especially, it can be more attractive in majority countries including Korea with high oil price than any other technologies because it is able to make light oil to be directly used for the industrial fuel.

Also recycling and reuse of plastic wastes have some disadvantages like classifying difficulties and the low quality of new product. Problems of storage and burning lead the countries to convert these wastes to electrical energy and some other chemical products by some chemical ways such as pyrolysis and hydrogenation. Some alternative ways of preventing the environmental pollution resulting from the plastic wastes can be listed as storing underground reprocesses converting to chemical products and/or generating energy by burning.

1.2.2 Pyrolysis Conditions for Recycling Plastics

Pyrolysis is the most common recycling technique converting plastic waste into fuels, monomers, or other valuable materials by thermal and catalytic cracking processes. It allows the treatment of mixed, unwashed plastic wastes. For many years research has been carried out on thermally converting waste plastics into useful hydrocarbons liquids such as crude oil and diesel fuel. Recently the technology has matured to the point where commercial plants are now available. Pyrolysis recycling of mixed waste plastics into generator and transportation fuels is seen as the answer for recovering value from unwashed, mixed plastics and achieving their desired diversion from landfill.

Polyethylene waxes obtained by pyrolysis were modified by the reaction of unsaturation with maleic anhydride in the amounts of 1-25% of polyethylene (GB Patent, 1037405, 1966).

Because of plastics remains undergraded for a long time and the places for burying these wastes are near limits it becomes impossible to use this method. And even it seems to be an economical way to get energy by burning these wastes, some special burning technology is needed and generating big air pollution are the disadvantages of burning them.

For several years, the feasibility of recycling commingled post-use polymers by pyrolysis has been a controversial subject. However several processes have been investigated in industry and recycling technologies based on fluidized bed pyrolysis have been studied extensively at the University of Hamburg. Research has focused on the suitability of plastic wastes, used tires, and oil residues as sources of well characterized purified olefins and other hydrocarbons. Pilot plants with capacity up to 120 kg/hr of used tires have been installed and a semi-industrial plant using the Hamburg process has been built in Germany by the Asea Brown Boveri Company. According to a recent report, the American Plastic Council is promoting pyrolysis as a viable form of chemical recycling.

Pyrolysis is a very versatile process, given that it allows for the simultaneous feed of a variety of wastes of polymeric nature (tyres, biomass, plastics and so forth) in order to upgrade them together. Furthermore, different operating strategies may be established in order for the products obtained to be used in different applications. Thus, there are two interesting variables in these strategies: operating temperature (thermal pyrolysis) and the use of catalysts (catalytic pyrolysis). Kinetic knowledge is essential for the determination of the optimum conditions for maximization of a given product and for the design and simulation of commercial reactors. In this sense, although polyethylene and polypropylene pyrolysis have been widely studied, the kinetic studies published in the literature are not suitable for reactor design, given that they are mostly studies carried out in a microreactor, under very different operating conditions to those of industrial reactors. Furthermore, the studies published up until now are simple approaches that exclusively describe the weight loss of the feed and, in the few studies that follow product formation, secondary reactions are not taken into account (although they are essential for a proper explanation of the experimental results), or a kinetic mechanism is proposed but no kinetic parameters are determined (Elordi et al., 2007)

Pyrolysis typically occurs under pressure and at operating temperatures above 430^{o}C (800^{o}F) (Çınar, 2000). In practice, it is not possible to achieve a completely oxygen-free atmosphere. Because some oxygen is present in any pyrolysis system, a small pyrolysis system, a small amount of oxidation occurs. Pyrolysis is not combustion but involves rather a complex set of reactions that depend both on the plastics involved and the precise nature of the thermolytic process used. Possible reactions pathways are:

- Decomposition into monomers
- Fragmentation of the principle chains into organic moieties of variable size, e.g. PE and PP.
- Simultaneous decomposition and fragmentation
- Elimination of simple inorganic moieties leaving charred residues, e.g. PVC
- Elimination of side chains, followed by crosslinking.

Pyrolysis has been studied on the thermal distillation of scrap tires into carbon black and pyrolytic oil. For a polymer recycling process to become successful, four important requirements must be met:

- scrap availability
- technology
- market for the product
- economics of the process

Four process technologies are currently being considered for chemical recycling:

- Cracking at 400-600^{o}C

- Gasification to produce mostly carbon monoxide and hydrogen.
- Hydrogenation under pressure to give mostly oil (syncrude)
- Pyrolysis around 500-900^{o}C to produce gaseous products

The co-pyrolysis of sawdust and polyethylene was studied and it was observed that there was interaction among the volatile components in the co-pyrolysis process (Dong et al., 2007).

1.2.3 Earlier Studies on Pyrolysis in Rubber Industry

The most common application of pyrolysis could be seen in tyre recycling processes.

Pyrolysis involves the thermal distillation of scrap tyres into carbon black and pyrolytic oil. The oil can be used as a feedstock for refining operations as though it were virgin crude, although it contains substantial contaminants. Pyrolysis is carried at temperatures in the range 450°C-900°C in the absence of oxygen. Whole tyres with an average weight of 20 kg. can be almost completely pyrolyzed (Scheirs, 1997).

As early as 1975, Goodyear developed a joint venture (TOSCO) to develop a facility for tyre pyrolysis. It was technically successful, though the economics were not viable. The gas generated in the process was utilized to fuel the plant while the resulting low-grade pyrolytic oil was marketable only as a crude oil blending material. Unfortunately, the carbon black/char was not acceptable for tyre production as it contained 20% ash (Goodyear publication, 1995).

Markets are still to be developed for the by-products of tyre pyrolysis as the char and oil products have not yet achieved the specifications required nor have they been economically priced. The quality of the carbon black at present is low because of the inorganic fillers from the tires (zinc oxide, carbonates and silicates) and the fact that the carbon componentis composed of a mixture of carbon blacks (up to ten different carbon blacks are present in a typical passenger tyre) (Serumgard and Blumenthal, 1995). Refinement procedures are being developed to increase the carbon black quality. The carbon black can be used as a modifier in asphalt roofing. It can also be used as a partial substitute for low reinforcing grades of carbon-black in rubber.

The pyrolytic oil is of a grade high enough to be fed back into the refinery process for making petroleum, diesel or lubricating oils. The pyrolytic oil contains high levels of aromatic hydrocarbons-benzene, toluene and xylene. For this reason, the oil is called “BTX” and is sold to chemical and plastics manufacturers.

The carbon char extracted directly from the pyrolysis process is generally of very low purity and can not be used in tyre manufacturing. However, recent advances in pyrolysis technology allow a high-grade carbon black is suitable for use in tyre manufacturing. This represents a significant advance because it actually allows closed-loop recycling of a proportion of scrap tyres.

Tyre pyrolysis plants are now in operation in British Columbia and Toronto (Unique Tire Recycling) with capacities of 800.000 tyres per year and also in South Korea (Tire Recycling Technologies Corp.) A tyre pyrolysis facility has recently been built in Alvsbyn, Sweden (by Atervinnings Bolaget). The pyrolysis reactor is from Beven Recycling (UK) and the char separation system has been purchased from American Tire Reclamation Inc. (Detroit USA).

A microwave reduction technique has been patented to decompose the tyres into useful products such as carbon black, diesel oil and steel. The process termed "reverse polymerization" takes place under anaerobic conditions in a nitrogen atmosphere. The absence of oxygen in the reactor suppresses formation of super-toxic compounds. The recovered diesel oil is used to generate electrical power. A pilot microwave reduction facility for scrap tyres has been operating in Toronto since late 1994 by the Environmental Waste Management Corporation. Considerable work on a microwave recycling process for scrap tyres has also been conducted by the Lawrence Plasma Laboratory.

1.2.4 The Importance of Pyrolysis in Polyethylene Recycling

Polyethylene (PE) plastic covers the largest percentage of the plastic family. Take China as an example. The yield of plastic in 1995 was 6 million tons and the PE product was 2.2 million tons. In 2000, the yield of plastic in China was 8 million tons and the PE product was 2.8 million tons. On the other hand, the content of PE waste in plastic wastes is 48%. This result shows that the additives in PE agricultural film will cause liver cancer in the human body. The increase of plastic waste and its harm has attracted the concern of the political and technological circles. Methods such as landfill, combustion, recycling, and pyrolysis were developed to eliminate plastic wastes, and pyrolysis is regarded as the best method. Three types of processes, pyrolysis, catalytic cracking, and pyrolysis-catalytic upgrade, were developed to convert PE waste plastic to oil. But since the molecular chain of PE is composed of -CH2-, the freezing point of the diesel obtained is very high and the research octane number of gasoline is very low, near 88. Thus it is not a feasible way to convert PE to oil. It is, however, a profitable way to convert PE waste to PE wax.

PE wax is a kind of polyethylene with a low molecular weight range (1000–4000). It has some special properties compared to common wax derived from petroleum, such as a high softening point, excellent distribution, flowing, water- and chemical-resistant properties, as well as good chemical stability. PE wax has a wide application field, such as lubrication, as an antimodule additive in the fabricating and processing of polyolefins and polyvinyl chloride (PVC) lubrication and dissipation for the dyes of plastic, anticorrosion in ink, antioxidation additive for rubber, shining for wood floors and cars, artificial candles, toys, painting cans, and so on. Most PE wax is made from the pyrolysis of PE resin, so the cost of PE wax is very high and the world market is in short supply. The technology of converting PE waste plastic to PE wax has a large potential market and a very strong competitive capability.

The understanding of the polyethylene (PE) pyrolysis is superficial and fragmentary. Conventionally, the kinetics of PE pyrolysis is described as a typical random chain scission. According to this theory, gaseous products, such as ethylene and ethane, are produced at the beginning of the pyrolysis with a rapidly decreasing polymerization degree (*n*) of PE. Actually, this theory only describes the situation at the end of the pyrolysis of PE, not the whole process. Furthermore, there are some deficiencies in the experimentation. Usually, PE is rapidly or slowly heated to a certain temperature and begins to decompose and emit gaseous products at this temperature. At the same time, the relation of polymerization degree to pyrolysis time and temperature are studied as well, and a kinetic model of pyrolysis is developed. In fact, PE begins its chain scission before this temperature, thus the traditional random chain scission theory of PE pyrolysis actually describes the pyrolysis behavior of the intermediates of PE pyrolysis, instead of the original PE. Furthermore, the traditional theory only describes the pyrolysis of the intermediate to final products, not including the pyrolysis of PE resin to the intermediates. As a result, this theory does not provide useful guidance for the heat treatment of PE resin and the optimal utilization of PE waste by pyrolysis.

Study on the conversion technology of polyethylene plastic to polyethylene wax showed melting ranges between 104 to 144 ^{0}C**,** the yield of the wax was over 90% (Shuyuan et al., 2003). Pyrolysis for the simultaneous generation of oils and gases to obtain hydrocarbons from waste plastics might supply crude petrochemicals. Nickel and rare earth metal exchanged Y-type zeolite catalyst (Ni-Rey) was used for producing light fuels (gasoline and kerosene) by the catalytic cracking of heavy oil from waste plastic in steam atmosphere.

Major suppliers of polyethylene waxes can be listed as Luxco wax (U.S.A), Honeywell Speciality Wax and Additives (U.S.A.), Sasol (Republic of South Africa), Micropowders Inc (U.S.A), Aldert Chemicals LTD (Canada), Britishwax (England), Iberceras (Spain), Waxchem (India), Guajarat Waxes (India), Zymöl (Poland), AGS Teknik Kimya Sanayi (Turkey).

1.2.5 Other Methods for Recycling Polyolefins

Plastic consumption, and consequently the amount of plastic waste, is growing year by year. According to figures released by the Association of Plastics Manufacturers in Europe in 1998, plastics consumption amounted to 30.4 million tonnes, consisting of 29.3 million tonnes of virgin polymer and 1.07 million tonnes of recycled granulate. The packaging sector remains the highest user of plastics, accounting for 41 wt.% of plastics consumed. Other users are building and construction 19 wt.%; household and domestic applications 18 wt.%; the automotive industry 7 wt.%; the electric and electrical industry 8 wt.%; the agricultural sector 3 wt.% and large industry for the remainder.

Polymers are subject to thermal degradation during their synthesis, storage, processing use as final product and reprocessing. These processes which gradually deteriorate the properties of polymers may include scission, branching and formation of crosslinks between polymer chains. The reaction of free radicals with oxygen produces peroxide radicals, which react with polymers forming hydroperoxides and other primary radicals that propagate chain reactions.

A high percentage of plastics end its lifetime as a part of the overall solid waste stream. The typical distribution of plastics in household waste is: polyolefins 66.9%, polystyrene 13.3%, PVC 10.3%, PET 5.3%, and others 4.2% (Kaminsky and Zorriqueta, 2007). Polyolefins as the main waste fraction consist of carbon and hydrogen only. This makes them extremely suitable for feedstock recycling with the production of valuable hydrocarbon products.

Thermal and catalytic treatments of polyolefins waste present meaningful differences. In terms of mechanism, thermal degradation proceeds a radical chain reaction pathway with hydrogen transfer steps. Normally, no rearrangement reactions occur, while branched products were only formed in secondary reactions as a result of the interaction between two radicals. As a consequence, thermal cracking of polyolefins leads towards a broad distribution of hydrocarbons up to waxy products. High temperatures of more than 500°C are needed to receive more oily products. In contrast, catalytic cracking takes place by lower temperatures and the formation of smaller hydrocarbons which are branched. This catalytic cracking can potentially lower costs and increase yields of valuable products.

Therefore, a great number of investigations in different research groups and reports were carried out using catalysts for the cracking of polyethylene and polypropylene. Numerous are the use of silica-alumina and zeolite catalysts for the pyrolysis of polyethylene. By these catalysts, the polymer chain could be shortened and the chain-branching increased. Ivanova et al. (1991) described the effects of Lewis acid catalysts ($AlCl_3$) on polyethylene cracking. They obtain much higher amounts of short hydrocarbons such as butenes, compared with a thermal cracking.

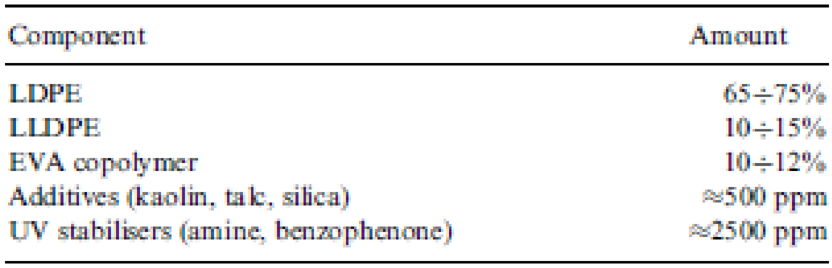
The role that unzipping, backbiting and random scission reaction pathways play in the evolution of low molecular species was probed. The model tracked 151 species and included over 11000 reactions. The model results were found to be in excellent agreement with experimental data for the evolution of condensable low molecular weight products (Levine and Broadbelt, 2009).

1.3 Mechanisms of Polymer Degradation

Thermal behavior of plastics can be improved by knowing thermal degradation kinetics. Many studies on pyrolysis kinetics of plastic wastes have been carried out, and also various reaction kinetic models are available to estimate plastic degradation, including integral method.

The degradation of the post-consumer material is investigated using infrared spectroscopy. For each class of material, virgin films and post-consumer films, the IR spectra are presented in Figure 1.3. The presence of the EVA copolymer gives rise to an absorption peak in the carbonyl region (1740 cm^{-1}). The effect of the UV exposure is, however, well evident because it strongly enhances this absorption peak, clearly indicating a significant photooxidation.

Table 1.1 Average composition of the greenhouse films*



Component	Amount
LDPE	65÷75%
LLDPE	10÷15%
EVA copolymer	10÷12%
Additives (kaolin, talc, silica)	≈500 ppm
UV stabilisers (amine, benzophenone)	≈2500 ppm

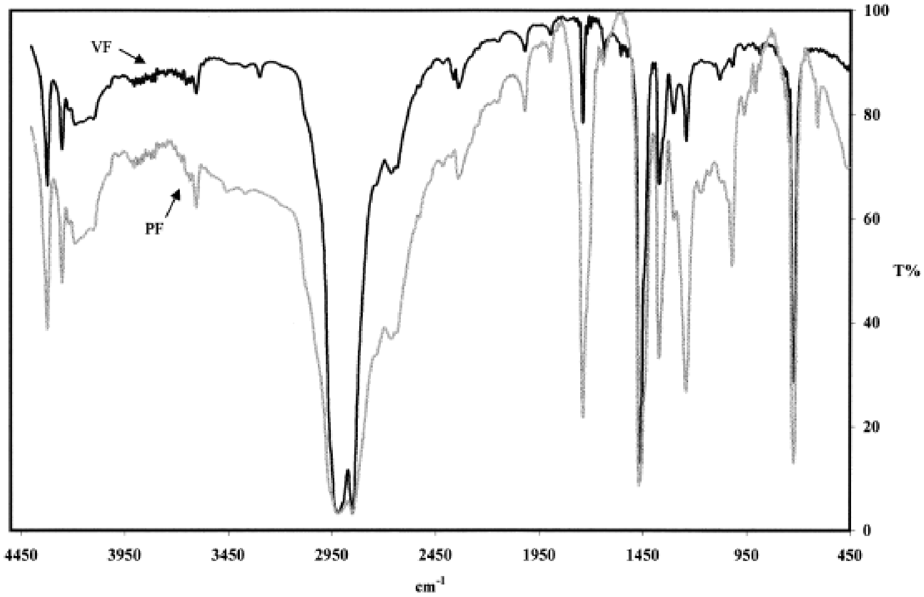


Figure 1.3 Infrared Spectra of Post-Consumer Film and Virgin Film**

The DSC analysis of the samples also proved that the post consumer film had undergone an appreciable degradation due to sunlight. In fact, the calorimetric curves showed larger values of the phase transitions enthalpies of post-consumer filmsamples with respect to virgin films and this is a sign of a larger crystalline content. Indeed, the post-consumer film crystalline content is higher than that of virgin films. This increased crystallinity can be ascribed to the lowering of the molecular weight of post-consumer film, if compared with virgin film, as a consequance of the photooxidative degradation. (Dintcheva et al., 2001)

A thermogravimetric analysis (TGA) technique is an excellent way for studying the kinetics of thermal degradation. It provides information on pre-exponential factor and activation energy. One of the materials in significant quantities in MSW is polyethylene wastes which consist of LDPE and HDPE. Thus, the objective of this work was just to study the thermal decomposition kinetics of these two kinds of plastic wastes which have the highest portion (~50%) of municipal and industrial plastic wastes in Turkey (Kayacan and Doğan, 2005-I).

* and ** is taken from (Dintcheva et al., 2001)

One of the materials in significant quantities in plastic wastes is polyethylene wastes which consist of LDPE and HDPE. Characterization of pyrolysis liquid products is evaluated in this work. This work includes the following two stages:

1. Pyrolysis of raw and waste LDPE and HDPE was carried out batch wise in a lab-scale fixed bed, and liquid products of the process were obtained.

2. Liquid products of the pyrolysis process were analyzed and characterized by using Fourier Transform Infrared Spectroscopy (FTIR), and Nuclear Magnetic Resonance (NMR) Analysis. FTIR spectroscopy provides measuring organic and inorganic functional groups, aliphatic and aromatic carbon and hydrogen. NMR analyses were used to determine carbon and hydrogen numbers in plastic samples (Kayacan and Doğan, 2005-II).

Low density polyethylene has a branched chain structure, whereas high density polyethylene has essentially a straight chain structure. Branched chain structure of LDPE lowers its degree of crystallinity and its density. The branched chain structure also lowers the strength of low density polyethylene. The molar masses of waxes are considerably lower than that of polyethylenes and plastics. Because polyethylene waxes are rather inexpensive, have improved applicability and consistency in quality, and are in constant supply they have displaced expensive natural waxes in many areas.

Possible mechanism of thermal degradation reactions in the absence of oxygen for PE is as follows:

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\ R \xrightarrow{\text{Initiation}} R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\bullet + R\bullet$$

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\bullet \xrightarrow{\beta\text{-scission}} R\text{-}CH_2\text{-}CH_2\bullet + CH_2{=}CH_2$$

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\bullet \xrightarrow{\text{Propagation}} CH_3\text{-}CH_2\text{-}CH{=}CH_2 + R\bullet$$

$$R\bullet + R\bullet \xrightarrow{\text{Termination}} R\text{-}R$$

Thermal degradation of polyethylene has been described as occurring by a random scission mechanism.

1.3.1 Kinetic Models of Mechanisms

For a mathematical proof, Simha–Wall equation can be used to draw an expression to show the deviation of kinetics of random scission degradation from a first-order reaction model (Gao et al., 2003)

For this purpose a relation is derived to determine reaction order from experimental experimental data of dynamic measurements. And this relation is applied to dynamic degredation of a high-density polyethylene. The reaction order thus determined is found to be consistent with that obtained from the isothermal measurements. The activation energy and pre-exponential factor of the dynamic degredation is also similar to those of the isothermal degredation.

For random scission degradation

$$\frac{dy}{dt} = A\exp\left(-\frac{E}{RT}\right) * (1-y) \tag{1}$$

holds true. And equation below is Simha–Wall equation.

$$1-\alpha = (1-y)^{L-1} * \left[1 + y * \frac{(N-L)*(L-1)}{N}\right] \tag{2}$$

where *y*, *N* and *L* are the fraction of bonds broken, the initial degree of polymerization and the least length of the polymer fragment not volatile, respectively and α is the degree of conversion or fractional conversion of the reaction. Differentiating with respect to time *t* and incorporating Eq. (1) leads to Eq. (3), which illustrates evidently that random scission degradation does not follow rigorously first-order kinetics.

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right) * L * \left[(1-\alpha) - (1-y)^{L-1}\right] \tag{3}$$

1.3.2 Proposal of Kinetic Mechanisms

Amongst the models in the literature, the one based on lumps is more suitable for reactor design, given that it allows for ascertaining the conditions for optimization of a given product or group of products. According to Westerhout et al., (1998) polyolefin thermal decomposition takes place following a random degradation mechanism, Figure 1.4 based on this fact, they are able to relate temperature to product formation.

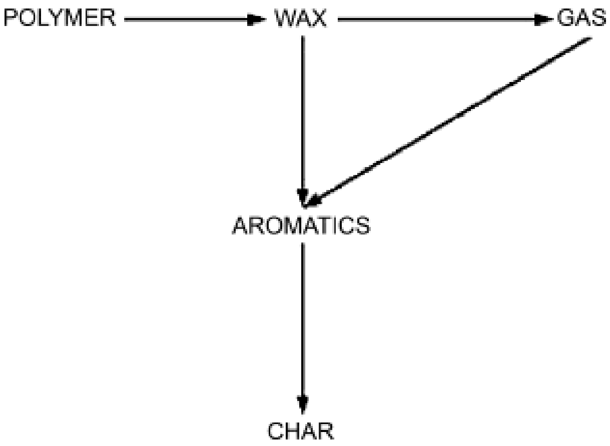


Figure 1.4 The kinetic scheme of a polymer mechanism

Several kinetic schemes are proposed in order to model the thermal pyrolysis of HDPE in a conical spouted bed reactor. Figure 1.4 clearly shows that the step of aromatic formation from gases is not significant in this case. Westerhout et al. (1998) proposed that waxes were the only primary product, but other authors (Horvat et al., 1999) also propose gases and liquid as primary products at low temperatures (around 400°C) at which pyrolysis begins to take place. The lump named liquid contains non-aromatic components. Accordingly, several kinetic schemes not based on that by Westerhout et al. (1998), but that have gases, liquid, waxes, aromatics and char as primary products, have been proposed. As an initial scheme, the one shown in Figure 1.5 has been proposed. In this kinetic scheme, all the lumps are obtained from the plastic.

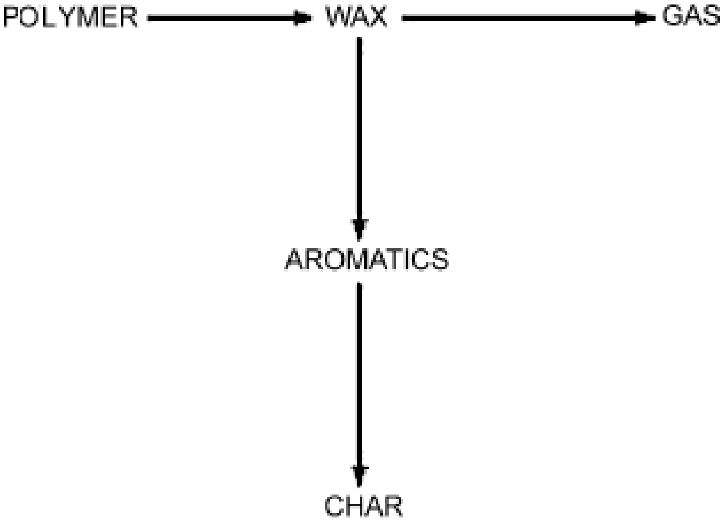


Figure 1.5 Kinetic scheme without the step of aromatics to gases

The experimental data obtained in this study shows that the formation of this fraction decreases as temperature is increased from high temperatures to higher ones, and then it turns to gaseous product at higher temperatures.

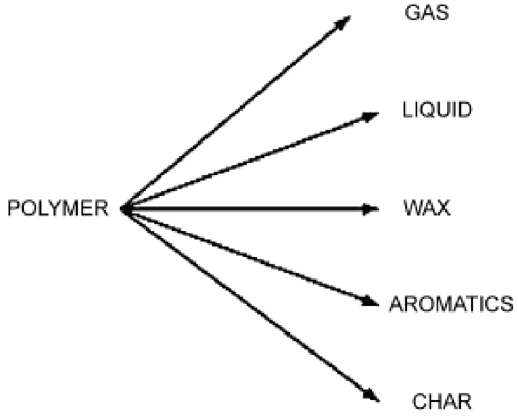


Figure 1.6 Kinetic scheme of parallel reactions

Consequently, the liquid fraction is formed following two steps, as a primary product at low temperatures, as was also observed by Horvat et al. (1999), and as a secondary product from the cracking of waxes. This is reflected in the kinetic scheme shown in Figure 1.6. The other kinetic schemes proposed, shown in Figure 1.7, contemplate that aromatics are also formed from waxes, as was also considered by Westerhout et al. (1998), or that they are only formed from waxes and not from the plastic.

It is well known that char is formed from aromatics, which have prompted the proposal of kinetic scheme in Figure 1.7, but char may also be formed only from aromatics, which is the case in kinetic scheme in Figure 1.7. Finally, a new step has been introduced for the formation of gases from waxes, last kinetic scheme in Figure 1.7.

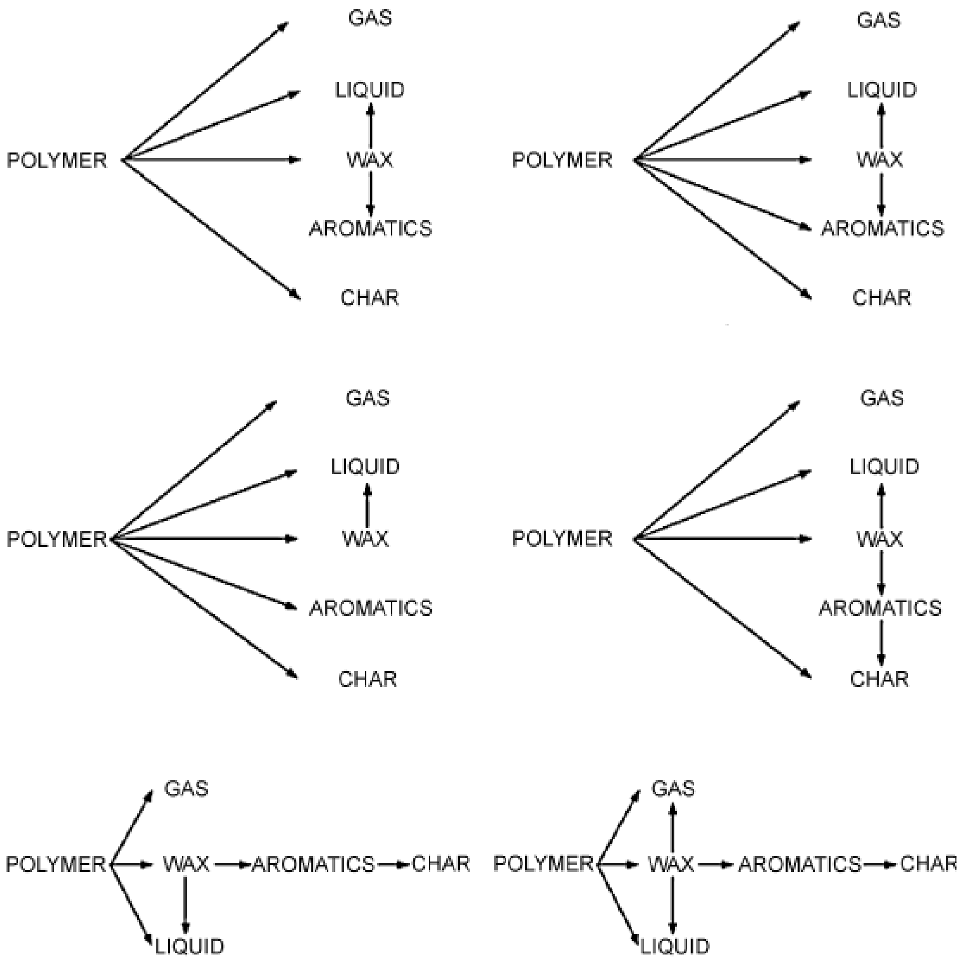


Figure 1.7 Kinetic schemes that consider secondary reactions

Random scission degradation may be described in terms of first-order kinetics when the number of chain scission is measured by change in the degree of polymerization. However, when random scission degradation is measured by weight loss, the kinetics will probably deviate from a first-order model. Since not every broken bond leads to the evaporation of a product, only product fragments which are small enough to evaporate will actually evaporate and thus lead to a decrease in the sample mass.

The modelling of the discontinuous pyrolysis process implies writing the kinetic equations for the formation of the different lumps and the consideration that at the end of the process the total amount of plastic has been degraded to give the different products. The amount of each lump formed up to a given time is calculated by integrating the mass evolution of this lump with time. Given that total conversion of the plastic is attained, the sum of all the lump masses at the end of the reaction must be the total mass of plastic in the feed:

$$M_0 = \sum_{i=1}^{n} \int_{t=0}^{t_f} \dot{m}_i \, \mathrm{d}t \tag{4}$$

The mass flow rate and yield of each lump are given by;

$$\dot{m}_i = M_0 \frac{\mathrm{d}X_i}{\mathrm{d}t} \tag{5}$$

$$X_i = \frac{M_i}{M_0} \tag{6}$$

Given that the reaction time in the conical spouted bed is very short (an average of 60–100 ms), the kinetic equations will not be written as a function of reactant concentrations within the reactor, but as a function of reactant formation rate corresponding to this step. Thus, the formation of a given lump is proportional to the formation rate of the reactant lump in this step. As an example, for the development of the model for the kinetic scheme of Westerhout et al. (1998), the kinetic equations for each lump are as follows:

- Wax: $\dot{m}_{\mathrm{W}} = \frac{\mathrm{d}X_{\mathrm{W}}}{\mathrm{d}t} M_0 = k_{\mathrm{PW}}(1 - X_{\mathrm{P}})M_0 - (k_{\mathrm{WG}} + k_{\mathrm{WA}})\frac{\mathrm{d}X_{\mathrm{W}}}{\mathrm{d}t} M_0$ (7)
- Gas: $\dot{m}_{\mathrm{G}} = \frac{\mathrm{d}X_{\mathrm{G}}}{\mathrm{d}t} M_0 = k_{\mathrm{WG}} \frac{\mathrm{d}X_{\mathrm{W}}}{\mathrm{d}t} M_0 - k_{\mathrm{GA}} \frac{\mathrm{d}X_{\mathrm{G}}}{\mathrm{d}t} M_0$ (8)
- Aromatics: $\dot{m}_{\mathrm{A}} = \frac{\mathrm{d}X_{\mathrm{A}}}{\mathrm{d}t} M_0 = k_{\mathrm{WA}} \frac{\mathrm{d}X_{\mathrm{W}}}{\mathrm{d}t} M_0 + k_{\mathrm{GA}} \frac{\mathrm{d}X_{\mathrm{G}}}{\mathrm{d}t} M_0 - k_{\mathrm{AC}} \frac{\mathrm{d}X_{\mathrm{A}}}{\mathrm{d}t} M_0$ (9)
- Char: $\dot{m}_{\mathrm{C}} = \frac{\mathrm{d}X_{\mathrm{C}}}{\mathrm{d}t} M_0 = k_{\mathrm{AC}} \frac{\mathrm{d}X_{\mathrm{A}}}{\mathrm{d}t} M_0$ (10)

By reordering this set of equations, the following set of differential equations is obtained :

$$\frac{\mathrm{d}X_{\mathrm{W}}}{\mathrm{d}t} = \frac{k_{\mathrm{PW}}}{1 + k_{\mathrm{WG}} + k_{\mathrm{WA}}}(1 - X_{\mathrm{P}}) \tag{11}$$

$$\frac{\mathrm{d}X_{\mathrm{G}}}{\mathrm{d}t} = \frac{k_{\mathrm{PW}} k_{\mathrm{WG}}}{(1 + k_{\mathrm{WG}} + k_{\mathrm{WA}})(1 + k_{\mathrm{GA}})}(1 - X_{\mathrm{P}}) \tag{12}$$

$$\frac{\mathrm{d}X_\mathrm{A}}{\mathrm{d}t} = \frac{k_\mathrm{PW}[k_\mathrm{WA}(1+k_\mathrm{GA})+k_\mathrm{WG}k_\mathrm{GA}]}{(1+k_\mathrm{WG}+k_\mathrm{WA})(1+k_\mathrm{GA})(1+k_\mathrm{AC})}(1-X_\mathrm{P}) \tag{13}$$

$$\frac{\mathrm{d}X_\mathrm{C}}{\mathrm{d}t} = \frac{k_\mathrm{PW}k_\mathrm{AC}[k_\mathrm{WA}(1+k_\mathrm{GA})+k_\mathrm{WG}k_\mathrm{GA}]}{(1+k_\mathrm{WG}+k_\mathrm{WA})(1+k_\mathrm{GA})(1+k_\mathrm{AC})}(1-X_\mathrm{P}) \tag{14}$$

The aim of this project is to investigate the pyrolysis of waste PE to produce a marketable product such as PE wax which finds use mainly in plastic injection and extrusion processes as lubricants.

2.0 MATERIALS AND METHODS

The polyethylene used in this project is supplied from a village of Buca named Kaynaklar area as scrap greenhouse polyethylene. Maleic anhydride is used as an initiator and it is supplied by Merck with the purity 99%. Its melting point is in the range between 50-53°C.

Simply the system used is like the scheme below.

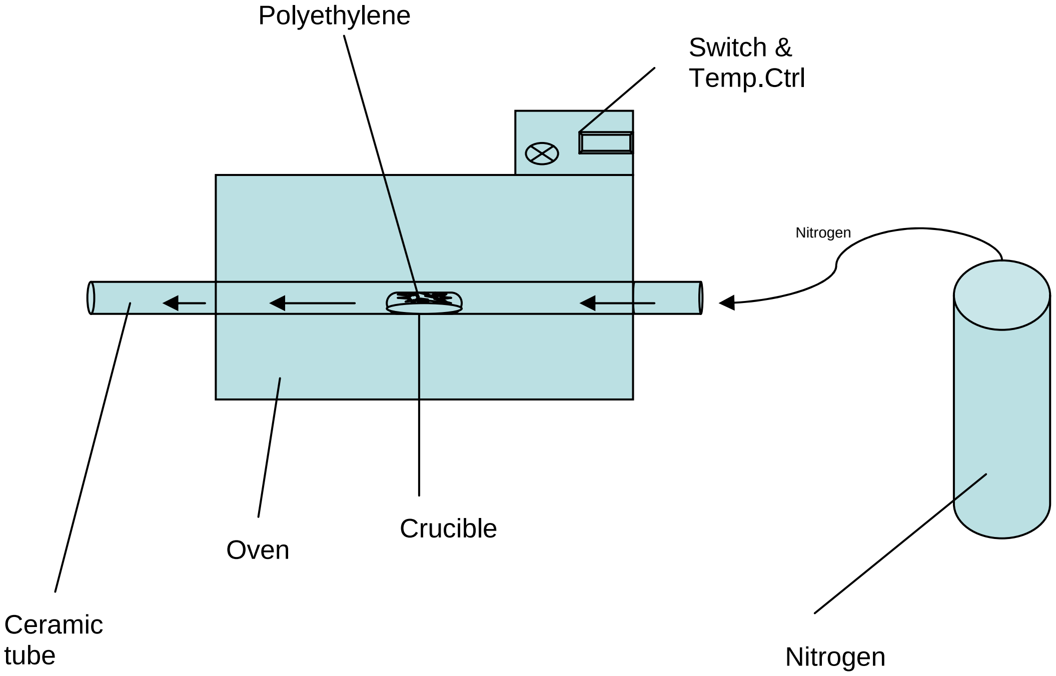


Figure 2.1 Experimental Set-up

A ceramic tube is placed in the heating medium and the crucible is located in the center of this tube where the heat can be supplied uniformly from every side of the oven.

Nitrogen gas is supplied from an external gas cylinder by measuring the flow rate of the gas through the tube to remove oxygen and maintaining an inert atmosphere in the pyrolysis tube. The flow rate is adjusted to 9.4 ml/min in all experiments.

The furnace used in all experiments is a trademark of Nuve and the experiments are carried out between the range of temperature 440°C and 480°C (+-3°C) and between the range of time 5 min. and 15 min. The temperature range and the duration of pyrolysis were chosen from the study made previously in this department (Tuna and Yenigül, 2003).

The **congealing point** of a wax is determined by applying a drop of molten wax to thermometer bulb, and noting the temperature at which it congeals (solidifies) when the thermometers rotated under standart cooling conditions (TS 4196 ISO 2207, 1999).

Another test applied to wax is **drop melting point** determination. The drop melting point of a wax is determined by recording the temperature at which a drop of the sample falls from the bulb of a thermometer when heated under standart conditions (TS 4367 ISO 6244, 1999).

FTIR : Spectrum-One FT-IR Spectrometer model of Perkin-Elmer with ATR module.

DSC : TA Instrument 2910 MDSC, V4, 4E from Polinas R8D laboratory. Thermograms were taken at 5°C/min heating rate and final temperature was adjusted to 150°C in air atmosphere.

3.0 RESULTS AND DISCUSSION

Experiments are carried out by using scrap greenhouse polyethylene film as starting material. About 1.0 g of this material is subjected to degredation between 440°C and 480°C for different time periods and the percentage of wax yield is determined. The results of these experiments are used for wax yield versus time graphics to be drawn.

Efficiency of wax production

Table 3.1 Wax yield

T(°C)/t (min)	5	6	7	8	10	12	15
440	84,34	78,12	71,47	66,32	55,92	46,42	29,08
445	82,02	76,25	70,14	63,81	52,76	40,98	19,81
450	78,47	72,77	66,30	61,84	48,01	34,56	11,38
455	75,36	69,99	62,45	57,98	43,55	28,04	7,17
460	73,23	68,31	61,11	55,31	41,31	24,73	5,11
465	71,09	64,55	58,15	51,93	40,08	23,03	4,01
470	67,52	63,03	55,53	49,75	38,27	21,54	3,23
475	66,12	59,85	51,48	46,85	35,63	18,82	2,14
480	62,16	57,82	48,78	44,07	32,21	15,86	1,42

According to these results, wax yield versus time graphics are constructed as in the following.

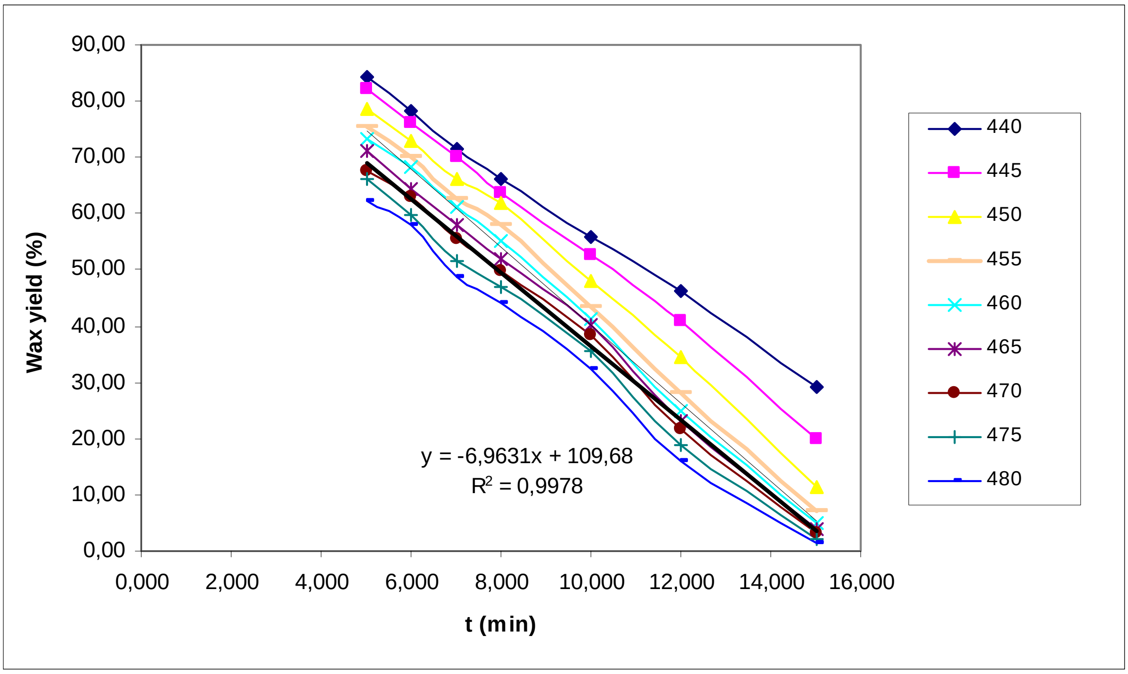


Figure 3.1 Wax yield versus time of PE Wax between 440°C and 480°C

It is observed in Table 3.1 that the yield of the waxes decrease as the time and temperature increase and the linearity between time and wax yield can be seen in Figure 3.1.

Congealing points of prepared waxes

Table 3.2 Congealing Point Values of PE Wax between 440°C and 480°C

Temperature (°C) / t (min)	5	6	7	8	10	12	15
440	104	102	101	100	99	97	95
445	104	102	100	99	97	95	94
450	104	102	100	98	96	93	91
455	103	102	101	99	97	95	92
460	99	98	97	95	93	90	89
465	102	100	99	98	95	94	92
470	101	100	98	97	95	93	91
475	100	99	97	96	94	92	90
480	99	97	96	95	94	92	90

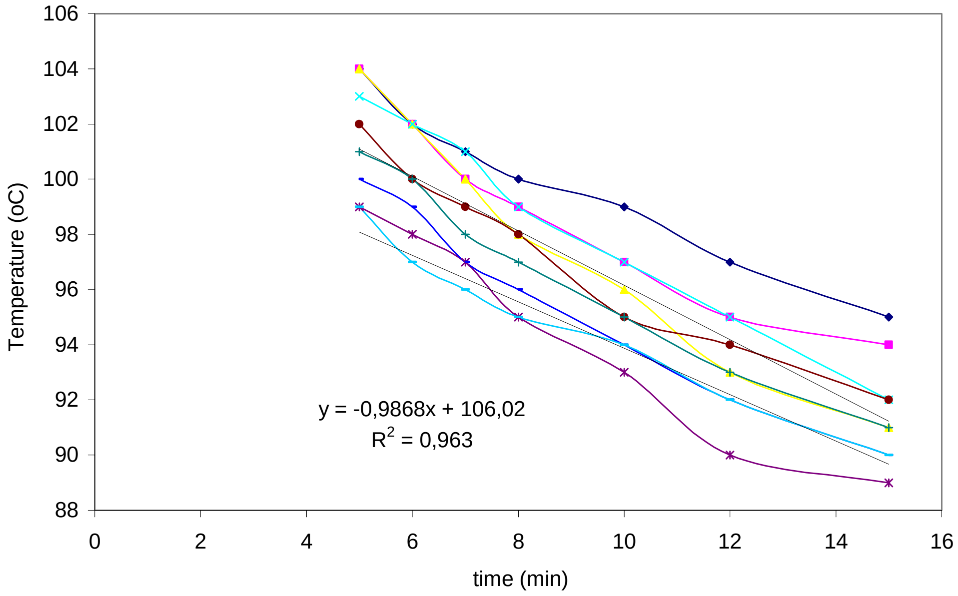


Figure 3.2. Time versus temperature of PE Wax for congealing point

Drop melting points of prepared waxes

Table 3.3 Drop Melting Point Values of PE Wax between 440°C and 480°C

Temperature (°C) / t (min)	5	6	7	8	10	12	15
440	112	110	109	108	106	105	104
445	111	109	108	107	107	105	104
450	112	111	110	109	107	106	104
455	113	112	110	109	107	105	103
460	111	109	107	105	103	101	99
465	112	110	108	106	105	103	102
470	110	109	107	106	105	103	101
475	108	107	106	104	103	102	100
480	108	106	105	104	103	101	99

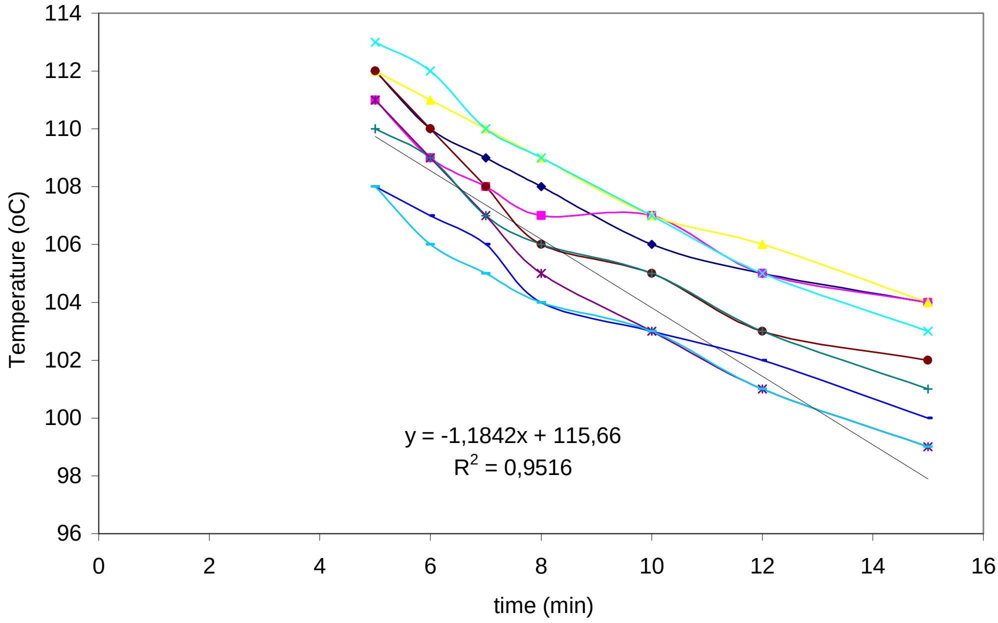


Figure 3.3 Time versus temperature of PE Wax for drop melting point

It is seen in Figure 3.2 that the congealing points (solidification temperature) of the waxes are decreasing as the time of pyrolysis increases. As the temperature increases it can be observed that the congealing point of a polyethylene wax has decreased.

Similar change can be seen in drop melting time and temperature graphs. The change can be observed in Table 3.3 and Figure 3.3.

In Figure 3.4 change of wax yield with temperature can be seen at 7 minutes.

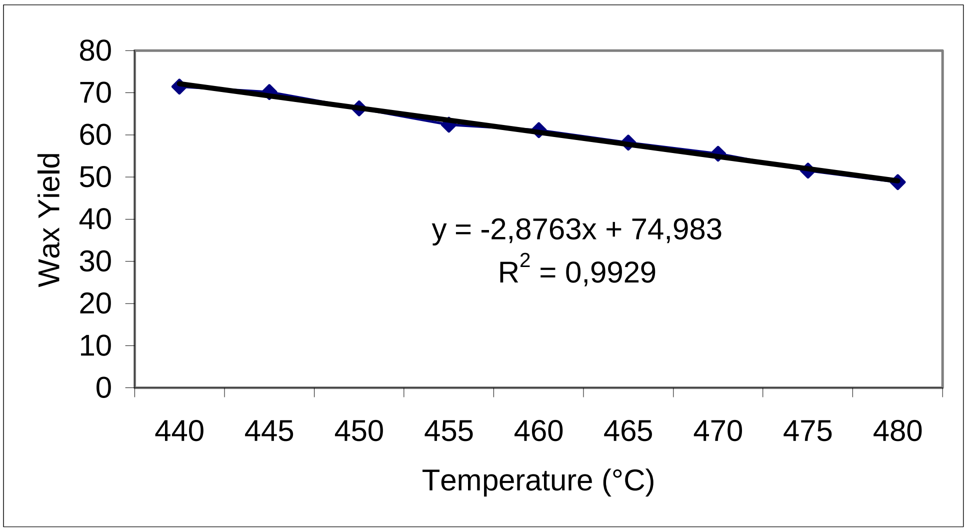


Figure 3.4 Wax yield versus Temperature at 7 minutes

FTIR spectra are taken for several pyrolysis products and the starting material which is waste polyethylene (Fig.B.1 to Fig B.7.) 1740 cm^{-1} peak mainly comes from oxidized polyethylene of the post-consumer films. But it is also known that greenhouse films may contain EVA copolymer which is seen in the same region up to 12%.

1900-2300 cm^{-1}, 3000 cm^{-1} and 675-995 cm^{-1} regions corresponds to unsaturation but as it is seen from the FTIR spectra it seems to be it is difficult to use the peak heights in quantitative measurements since unsaturation is negligible in these solid pyrolysis products. Maleic anhydride modified pyrolysis product showed similar spectrum, it is understood that a slight reaction occurs between unsaturated wax and maleic anhydride at specified conditions.

Kinetic study made by Westerhout et al. (1998) showed us that the pyrolysis process is highly complicated one as it is seen for different rate constants in equations 11-14, since four products wax, gas, aromatics and char are the main products of the process. In this study mass changes for four products are followed by changing time and temperature. In our study, it is focused on the formation of waxy compounds, its yield and properties of the products.

Table 3.4 DSC Results of PE and waxes

	Melting Point (°C)	ΔHu(J/g)
Starting material	108.81 and 116.57	378.6
450°C and 10 min.	112.73	125.5
460°C and 7 min.	105.96	84.5
465°C and 8 min.	109.58	102.6
160°C and 1 hour (maleization process of 465°C and 8 min.)	104.01 and 109.06	64.88

In DSC thermograms two melting peaks are observed in the waste polyethylene which is used as a starting material in all pyrolysis experiments. One of the peaks probably comes from the LLDPE which is used in greenhouse films up to 15%.

In the figure C.3, DSC thermogram 116.57°C of the starting material melting temperature shifts to 105.96°C which is obtained at 460°C and 7 minutes. This result is expected since low molecular weight polymers melt at lower temperatures than high molecular weight polymers as given by

$$1/T_m - 1/T_m(\infty)=2RM_o/\Delta H_u M_n$$

In this equation T_m is the melting point in Kelvin of polymers with a number average molecular weight M_n. Polymer of infinite molecular weight melts at $T_m(\infty)$. The molecular weight of the monomeric unit is M_o. R the gas constant and ΔH_u the heat of fusion per mole of crystalline polymer repeating unit (Nielsen and Landel, 1994)

It is known that pyrolysis causes the formation of unsaturation in the wax products and this unsaturation are needed to be saturated with some double bond containing monomers like maleic anhydride. The thermogram can be seen in Figure C.5 and melting point seems to be constant during maleization process which is 109.06°C.

The thermograms are very broad which means that melting range is high and this can be explained by the random chain scission degredation of polymer chains. In Figure C.5 second peak appeared which corresponds to maleized PE wax portion of the mixture and low value of ΔH_u can be attributed to the degredation of the crystal structure.

4.0 CONCLUSION

The recycling of post-consumer films for greenhouses is strongly dependent on the initial structure of the plastic materials and on the processing conditions. The films contain small amounts of low molecular weight compounds probably coming from the photooxidation of the PE molecules and from the absorption of fertiliser and pesticide residues. The amount of these compounds is, however small and does not prevent the use of the recycled materials in many applications.

The products of PE pyrolysis, solids and/or liquids and gases are obtained depending on the process temperature and time. As the pyrolysis temperature increases, the gas production increases while oil and wax production decreases. Although the wax yield is high at short time, the wax obtained is quite similar in congealing and drop melting temperatures of polyethylene itself. When PE decomposes to PE wax, it will decompose like that of heavy oil, that is to say, the common random chain scission theory of PE pyrolysis is followed.

Drop melting and congealing temperatures are obtained by using standard techniques. Temperature and time strongly effects the properties of the waxes obtained. Congealing temperatures of the waxes are changing between 90°C and 104°C. Drop melting temperatures of the waxes are changing between 99°C and 113°C.

Table 4.1 Congealing and Drop Melting Points of the Commercial Wax

	Commercial wax
Congealing Temperature(°C)	94
Drop melting Temperature(°C)	108

It is seen in Table 4.1 that the obtained values of congealing and drop melting temperatures are similar with the commercial one. As far as wax quality is concerned the best condition for the pyrolysis of greenhouse polyethylene is 460°C and 7 minutes with the operating system explained before.

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6.0 APPENDICES

6.1 APPENDIX A

Efficiency of wax production

Table A.1 Wax yield at 440°C

440°C

t (min)	5	6	7	8	10	12	15
Mi (gram)	0,999	0,995	1,008	1,000	0,999	0,997	1,000
Mf (gram)	0,842	0,777	0,720	0,664	0,559	0,463	0,291
Wax yield%	84,34	78,12	71,47	66,32	55,92	46,42	29,08

Table A.2 Wax yield at 445°C

445°C

t (min)	5	6	7	8	10	12	15
Mi (gram)	0,999	1,002	1,000	1,001	1,000	0,996	1,001
Mf (gram)	0,819	0,764	0,702	0,638	0,527	0,408	0,198
Wax yield%	82,02	76,25	70,14	63,81	52,76	40,98	19,81

Table A.3 Wax yield at 450°C

450°C

t (min)	5	6	7	8	10	12	15
Mi (gram)	0,996	1,000	1,000	1,000	0,999	0,993	1,003
Mf (gram)	0,781	0,728	0,663	0,618	0,480	0,343	0,114
Wax yield%	78,47	72,77	66,30	61,84	48,01	34,56	11,38

Table A.4 Wax yield at 455°C

455°C

t (min)	5	6	7	8	10	12	15
Mi (gram)	1,001	1,002	1,006	1,000	0,998	0,996	1,000
Mf (gram)	0,754	0,701	0,628	0,580	0,435	0,279	0,072
Wax yield%	75,36	69,99	62,45	57,98	43,55	28,04	7,17

Table A.5 Wax yield at 460°C

460°C

t (min)	5	6	7	8	10	12	15
Mi (gram)	0,999	0,997	1,000	1,009	0,997	1,005	1,008
Mf (gram)	0,731	0,681	0,611	0,558	0,412	0,249	0,052
Wax yield%	73,23	68,31	61,11	55,31	41,31	24,73	5,11

Table A.6 Wax yield at 465°C

465°C

t (min)	5	6	7	8	10	12	15
Mi (gram)	0,997	1,009	1,002	1,005	0,997	1,006	1,001
Mf (gram)	0,709	0,651	0,583	0,522	0,399	0,232	0,040
Wax yield%	71,09	64,55	58,15	51,93	40,08	23,03	4,01

Table A.7 Wax yield at 470°C

470°C

t (min)	5	6	7	8	10	12	15
Mi (gram)	1,009	0,991	1,007	1,005	0,999	1,001	1,003
Mf (gram)	0,681	0,625	0,559	0,500	0,382	0,216	0,032
Wax yield%	67,52	63,03	55,53	49,75	38,27	21,54	3,23

Table A.8 Wax yield at 475°C

475°C

t (min)	5	6	7	8	10	12	15
Mi (gram)	0,996	1,003	1,000	1,006	0,996	0,997	1,003
Mf (gram)	0,659	0,600	0,515	0,472	0,355	0,188	0,022
Wax yield%	66,12	59,85	51,48	46,85	35,63	18,82	2,14

Table A.9 Wax yield at 480°C

480°C

t (min)	5	6	7	8	10	12	15
Mi (gram)	1,001	1,000	0,997	0,998	1,006	0,991	1,007
Mf (gram)	0,622	0,578	0,487	0,440	0,324	0,157	0,014
Wax yield%	62,16	57,82	48,78	44,07	32,21	15,86	1,42

6.2 APPENDIX B

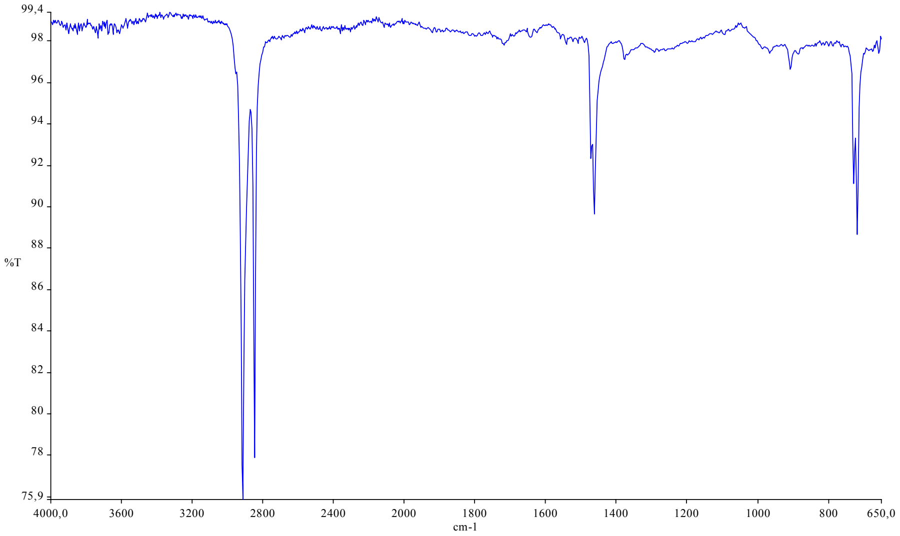

Figure B.1 FTIR Spectrum of greenhouse polyethylene before pyrolysis

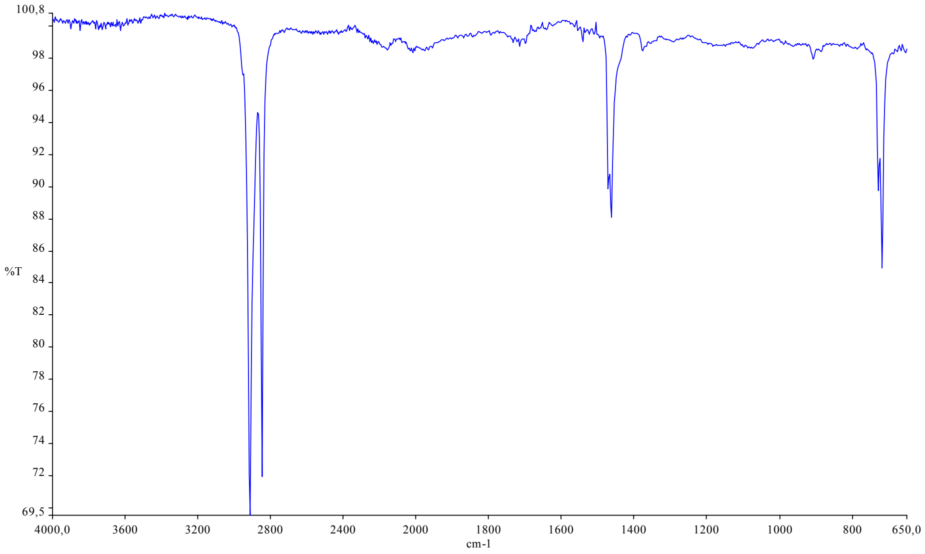

Figure B.2. FTIR Spectrum of polyethylene wax at 445°C and 10 min.

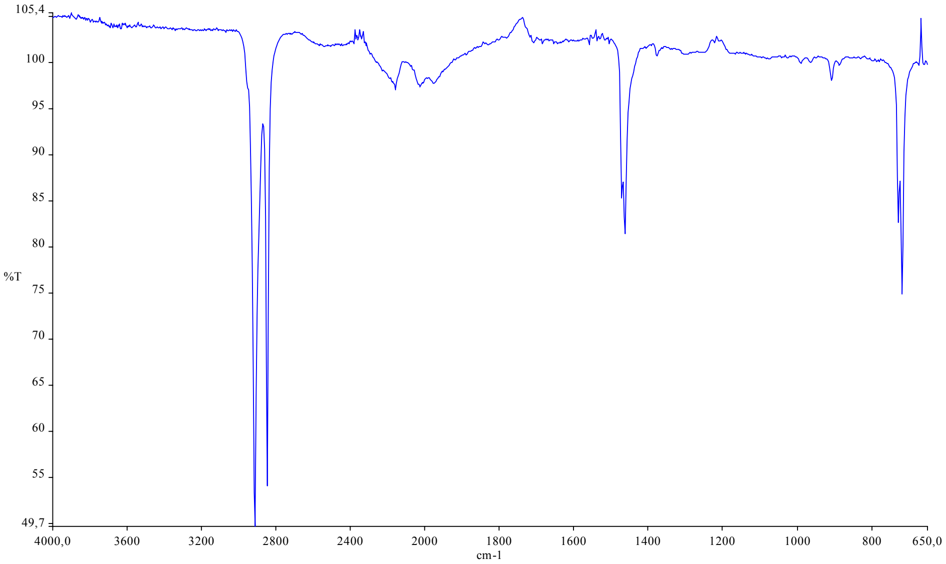

Figure B.3. FTIR Spectrum of polyethylene wax at 450°C and 8 min.

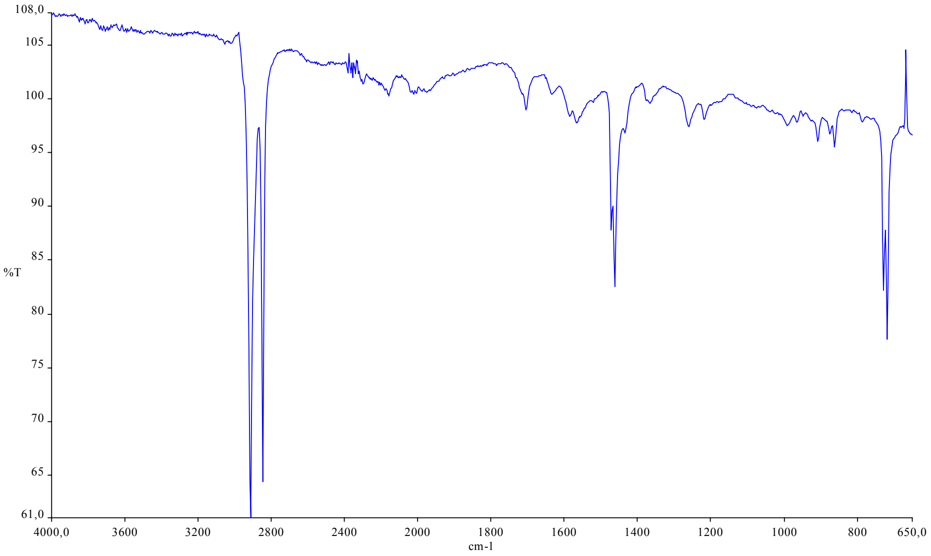

Figure B.4. FTIR Spectrum of polyethylene wax at 460°C and 7 min.

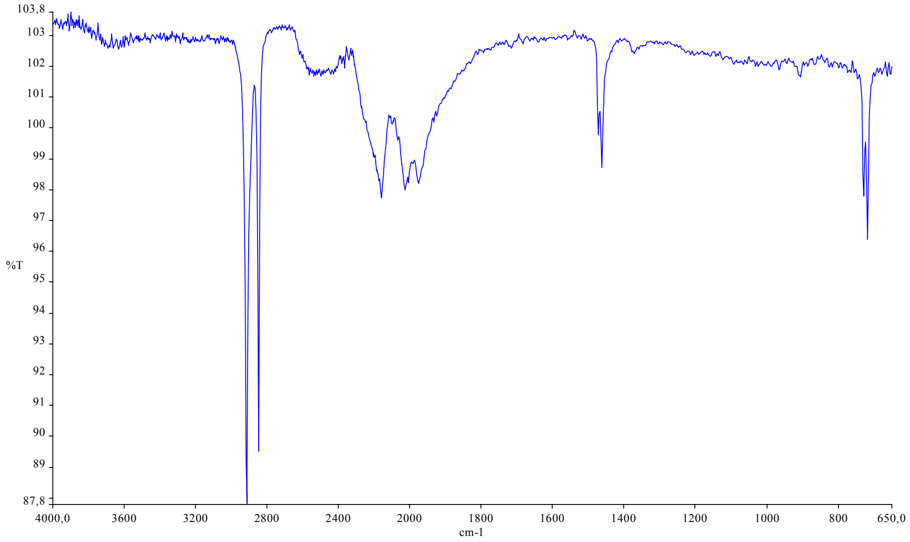

Figure B.5. FTIR Spectrum of polyethylene wax at 470°C and 6 min.

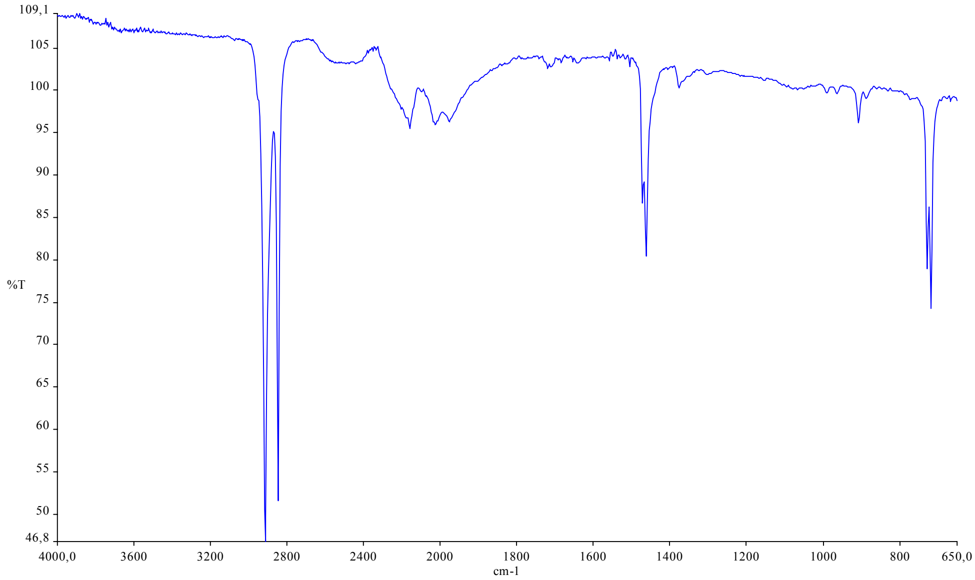

Figure B.6. FTIR Spectrum of polyethylene wax with maleic anhydride at 160°C and 1 hour.

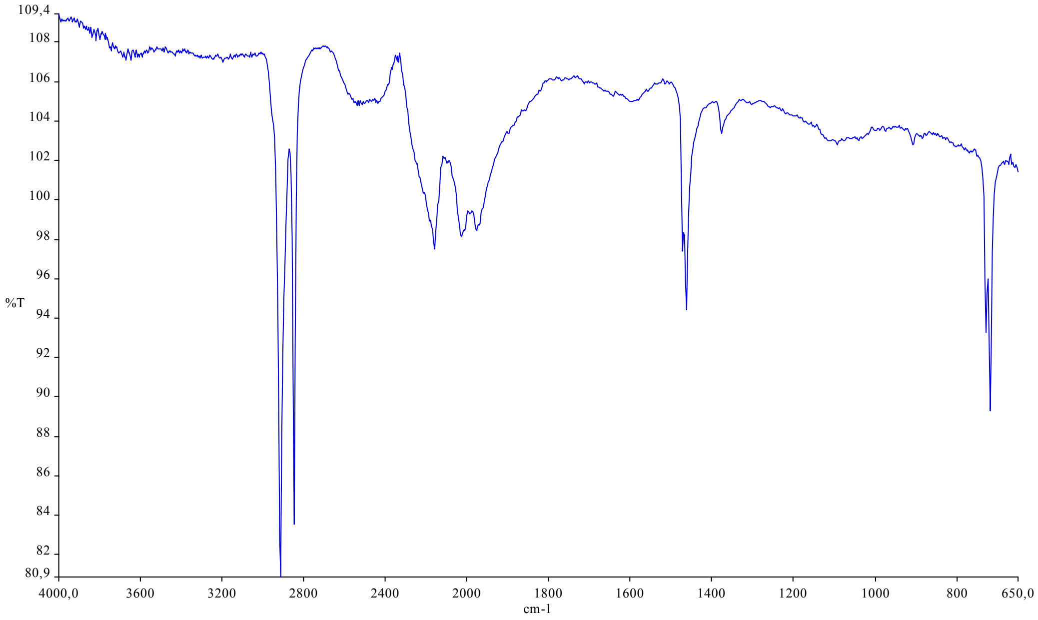

Figure B.7. FTIR Spectrum of polyethylene wax with maleic anhydride at 170°C and 1 hour.

6.2 APPENDIX C

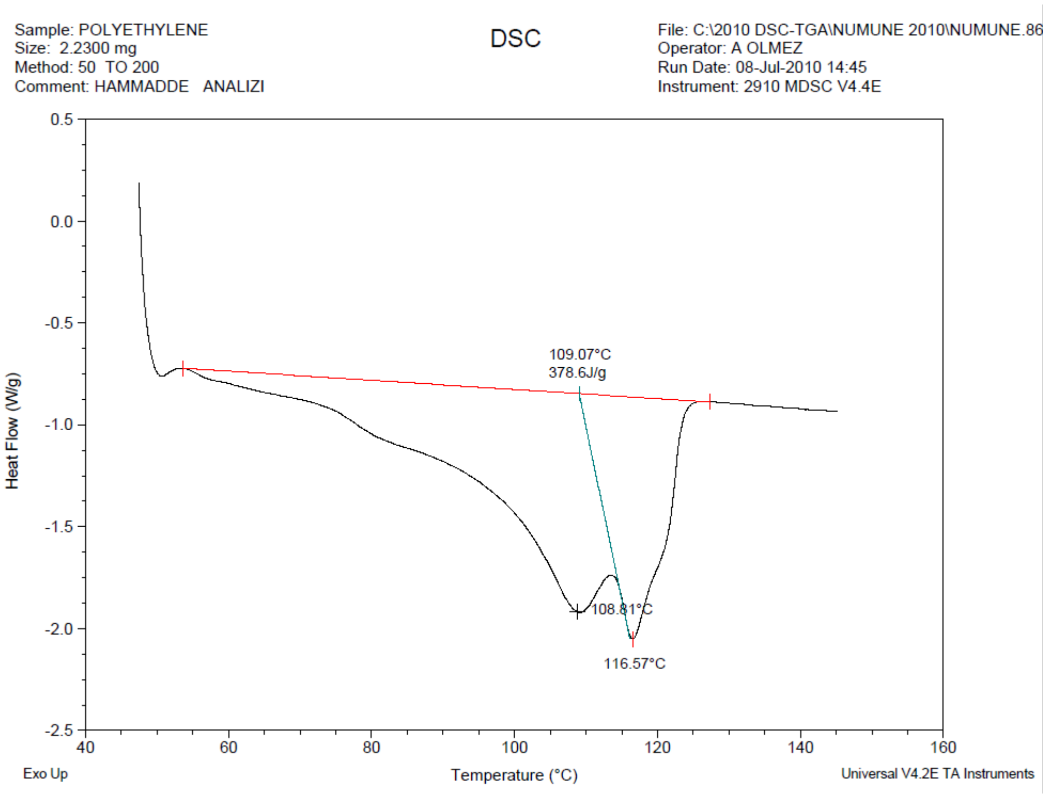

Figure C.1. DSC Spectrum of a greenhouse polyethylene film

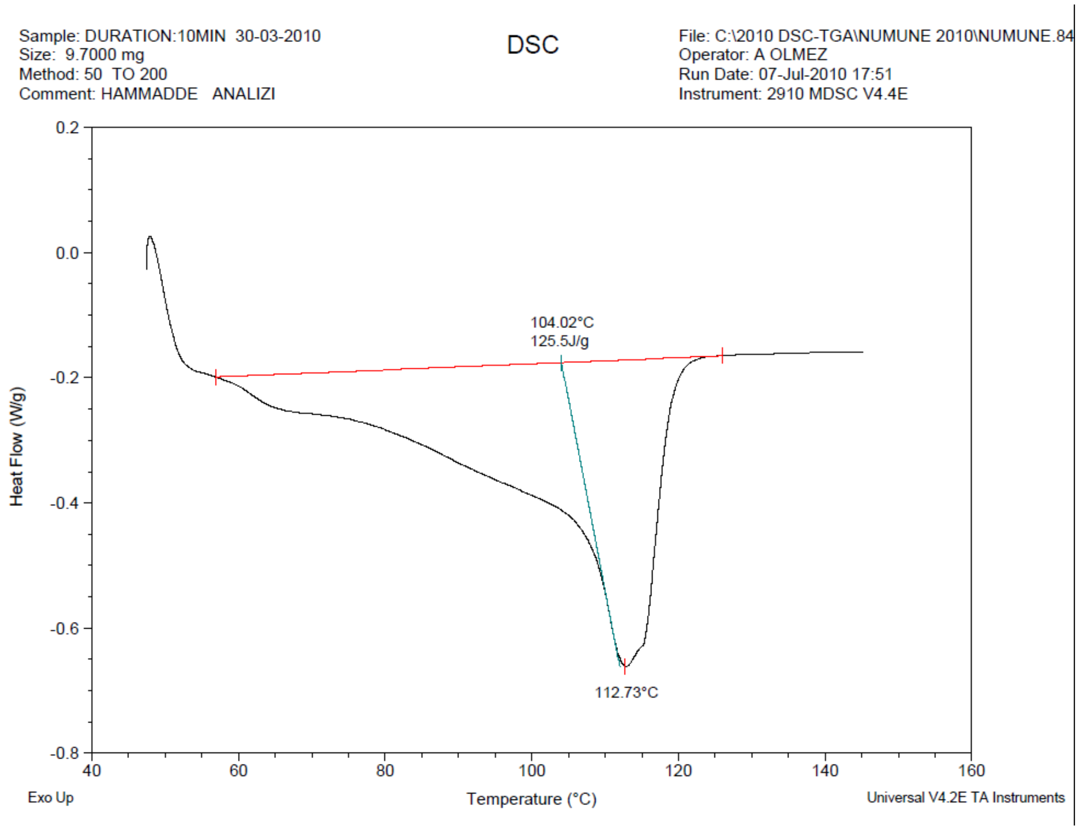

Figure C.2 DSC Spectrum of a PE wax under pyrolysis at 450°C and 10 min

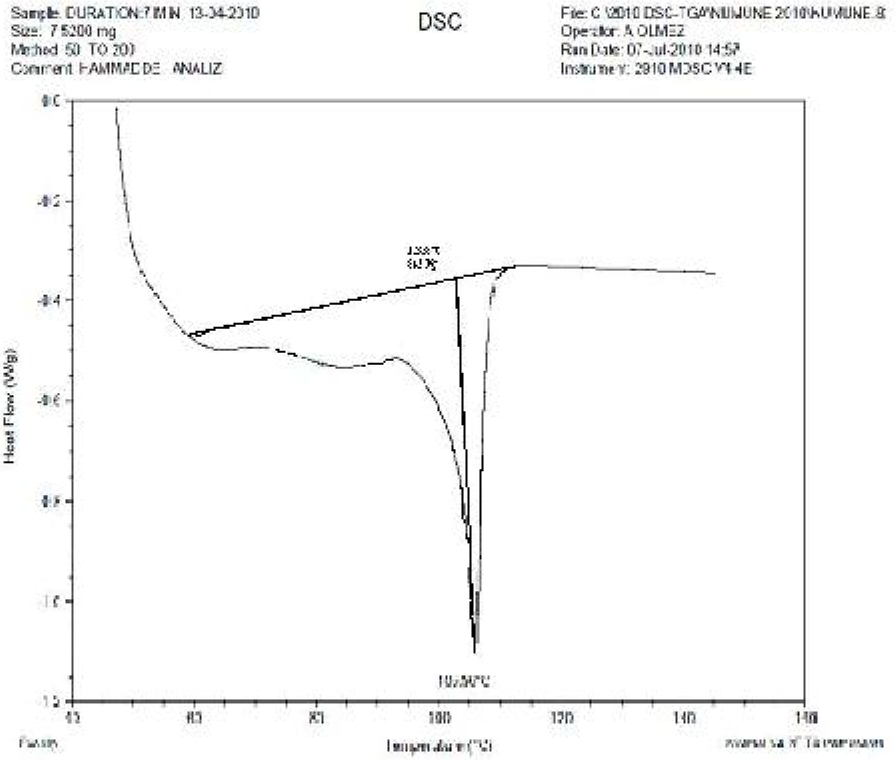

Figure C.3 DSC Spectrum of a PE wax under pyrolysis at 460°C and 7 min

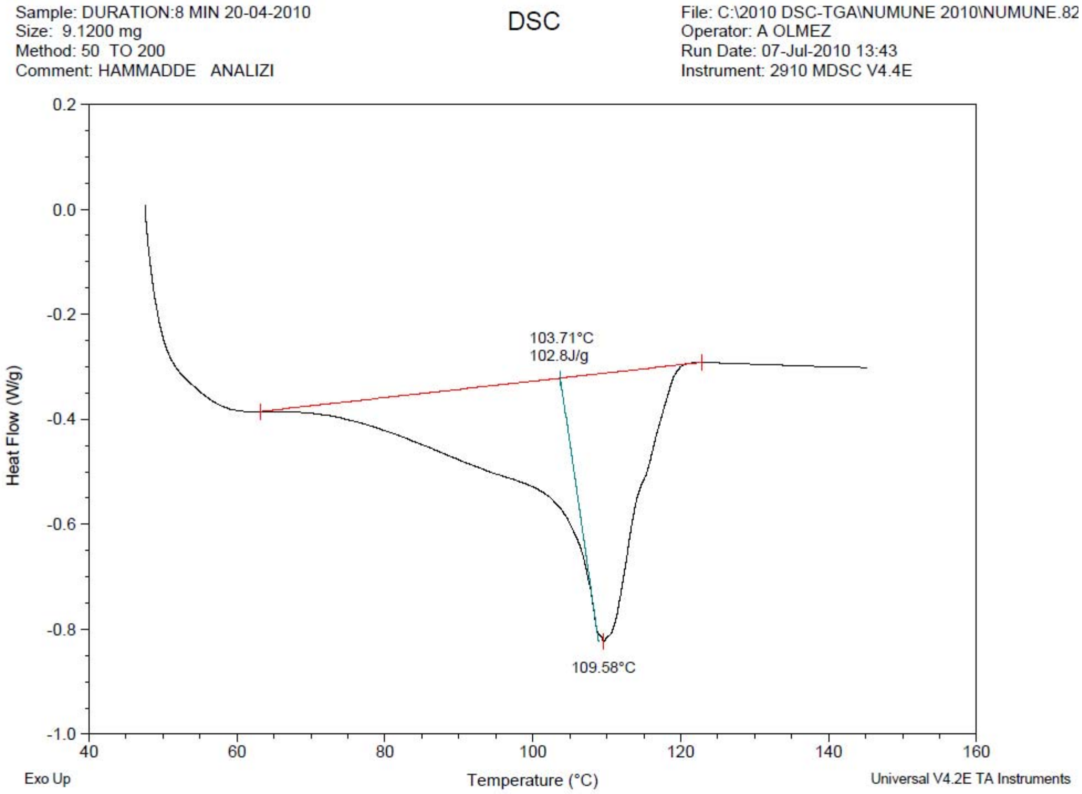

Figure C.4 DSC Spectrum of a PE wax under pyrolysis at 465°C and 8 min

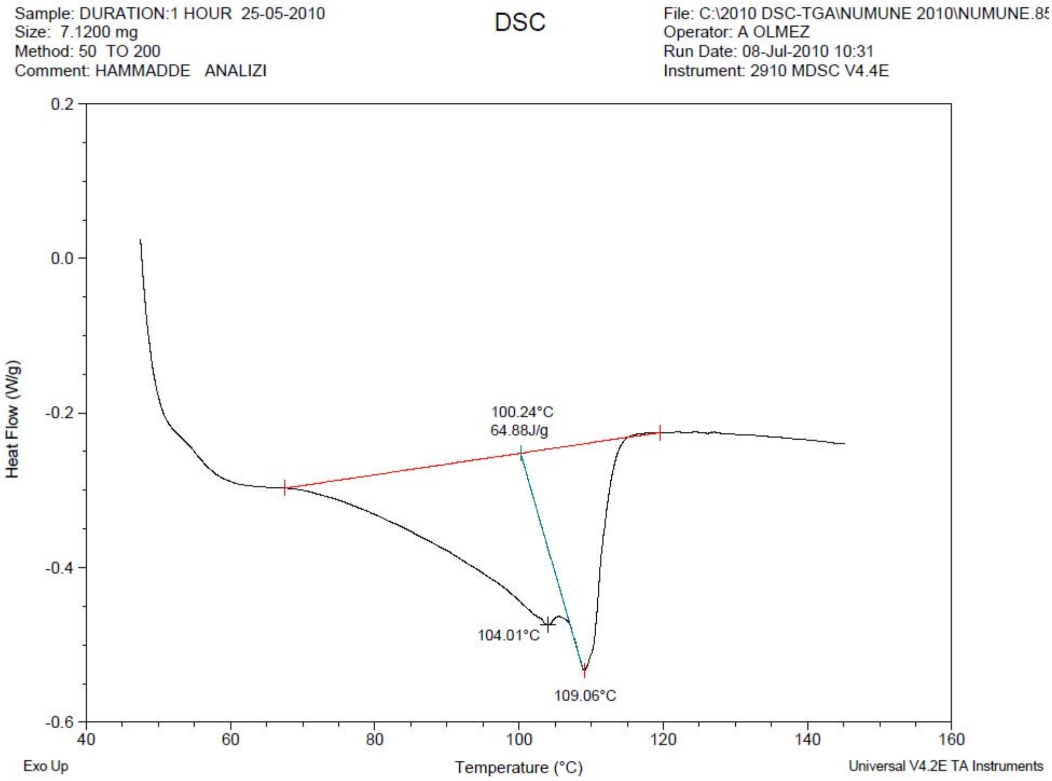

Figure C.5 DSC Spectrum of a PE wax with maleic anhydride at 160°C and 1 hour

APPENDIX D

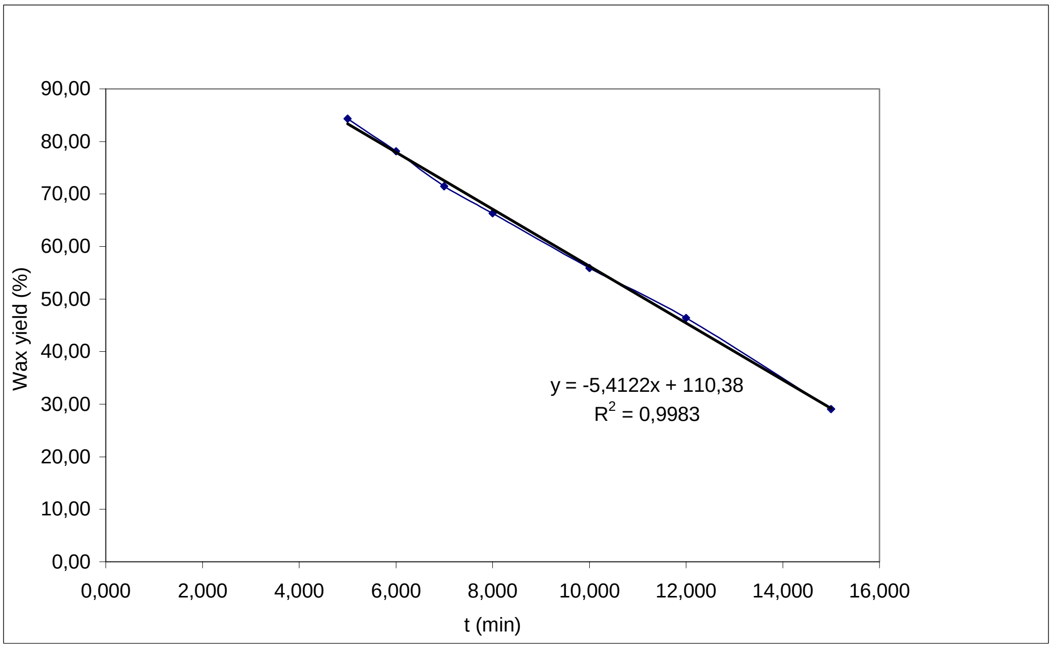

Figure D.1 Wax yield versus time of PE Wax at 440°C

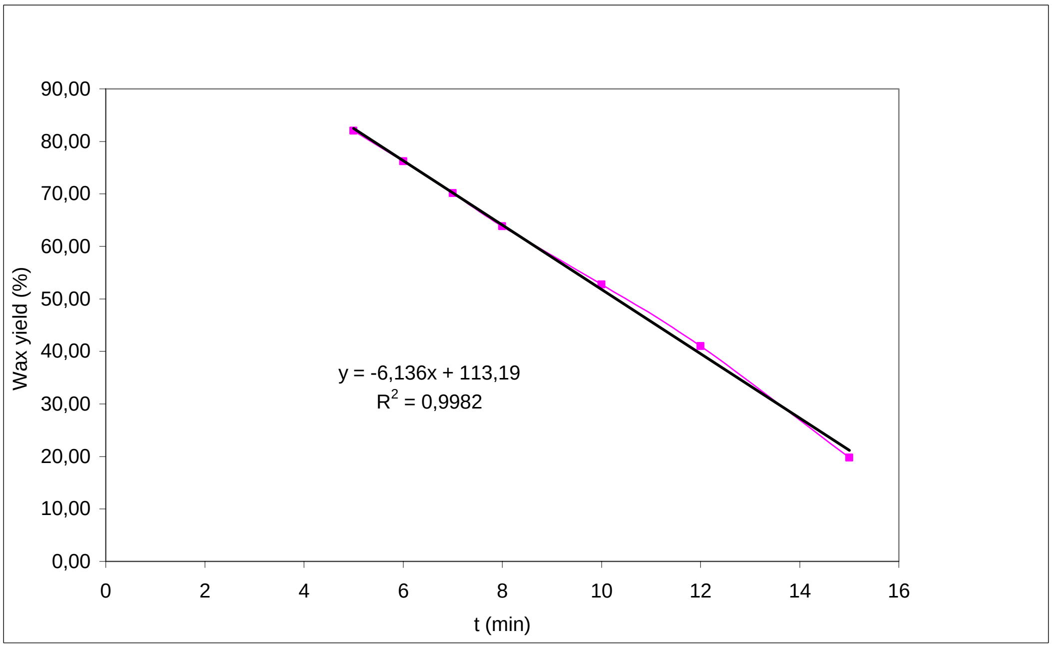

Figure D.2 Wax yield versus time of PE Wax at 445°C

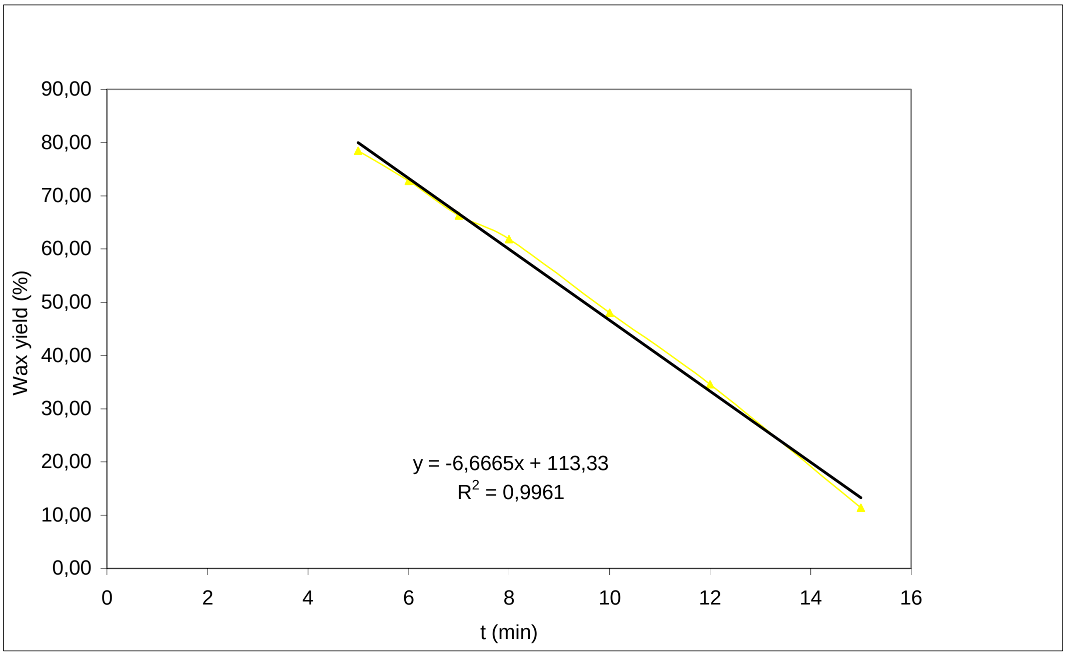

Figure D.3 Wax yield versus time of PE Wax at 450°C

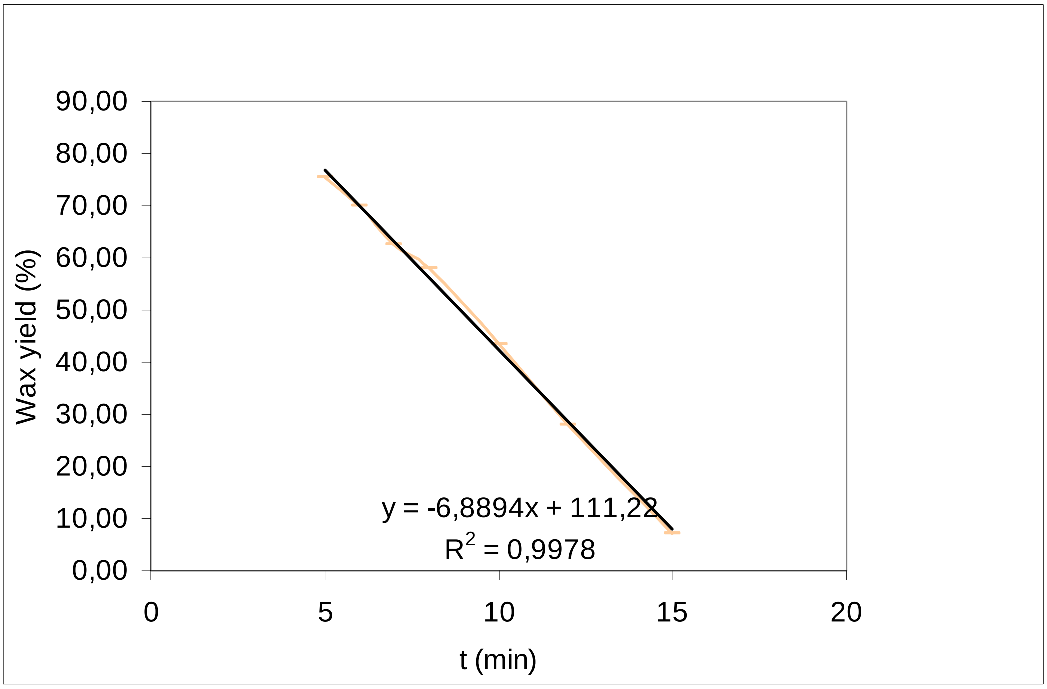

Figure D.4 Wax yield versus time of PE Wax at 455°C

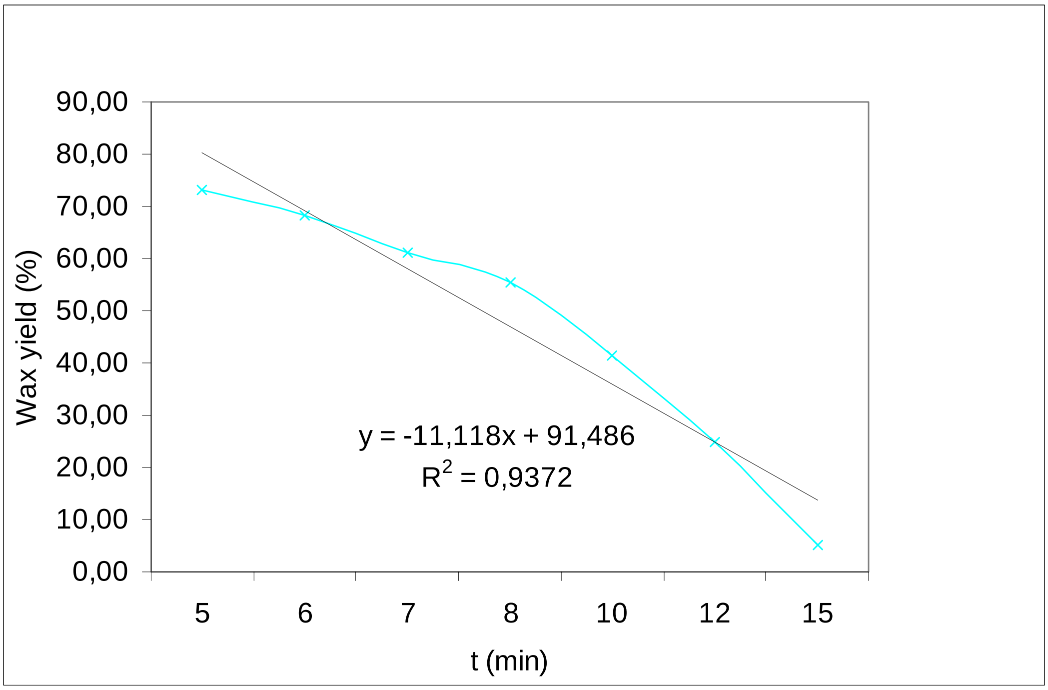

Figure D.5 Wax yield versus time of PE Wax at 460°C

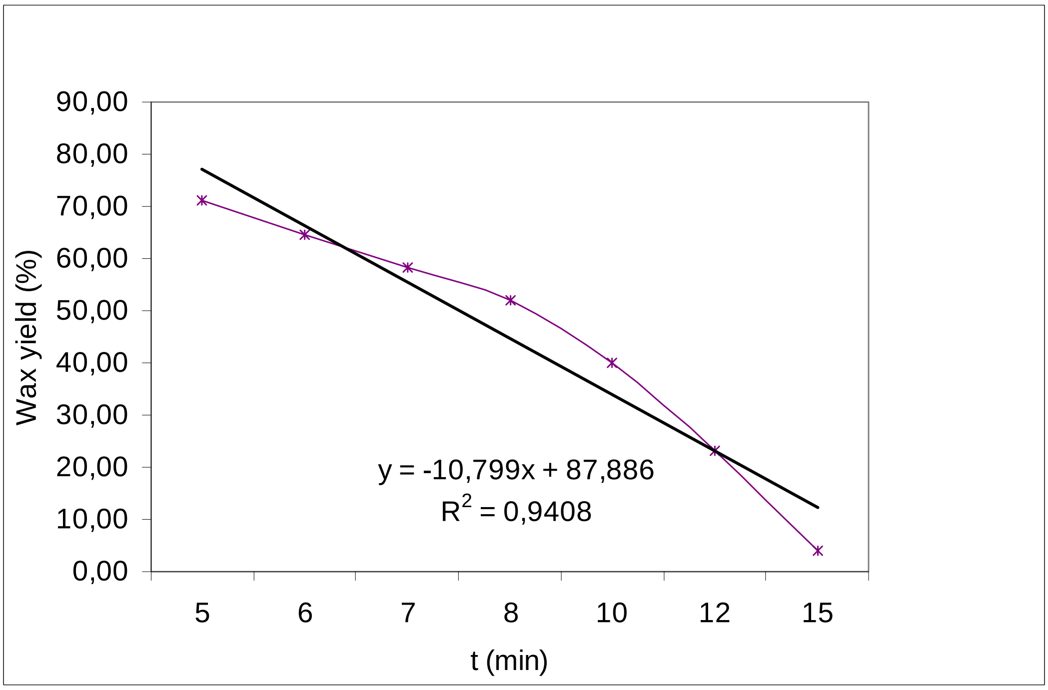

Figure D.6 Wax yield versus time of PE Wax at 465°C

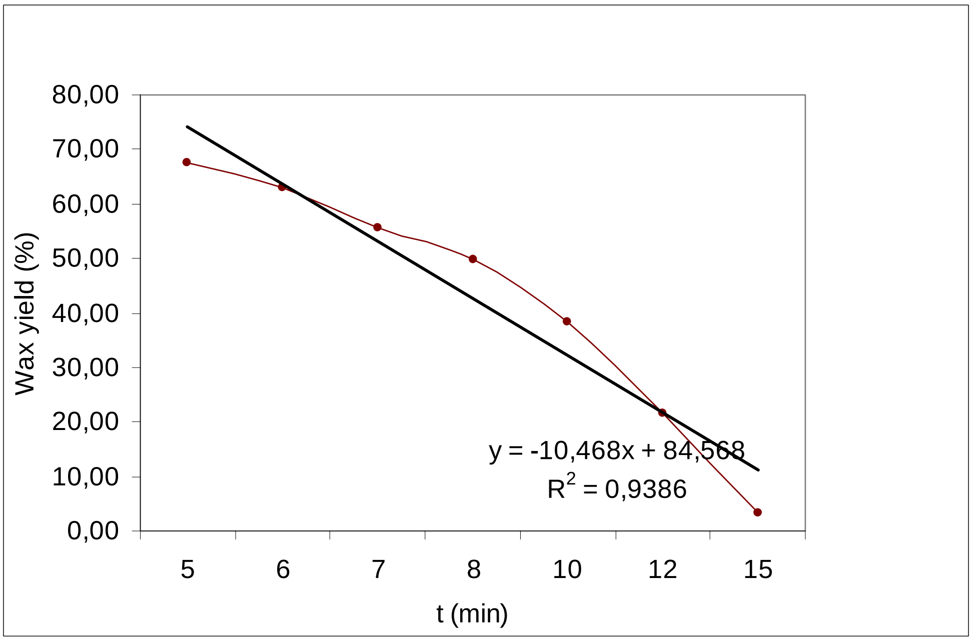

Figure D.7 Wax yield versus time of PE Wax at 470°C

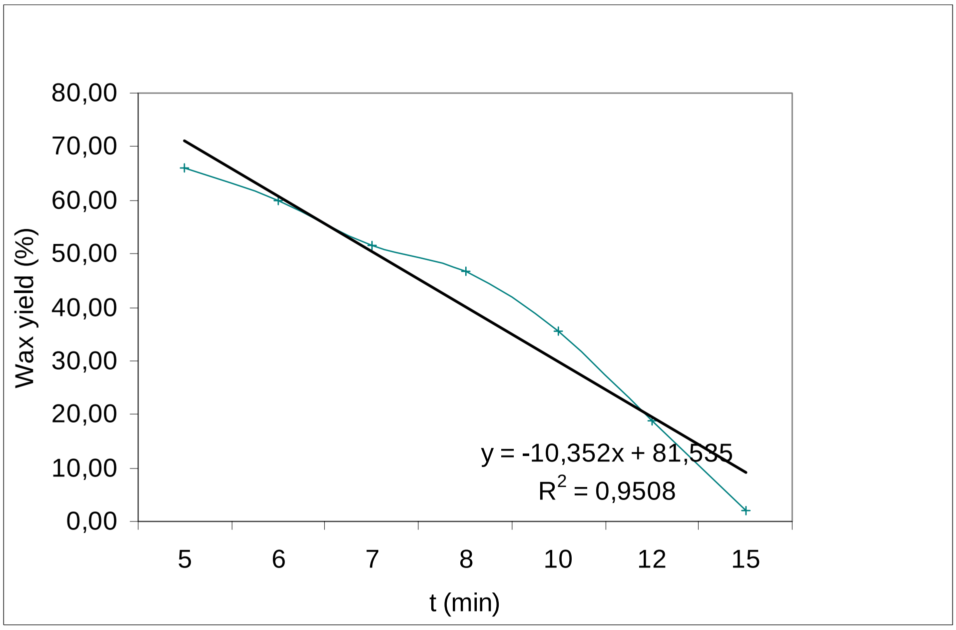

Figure D.8 Wax yield versus time of PE Wax at 475°C

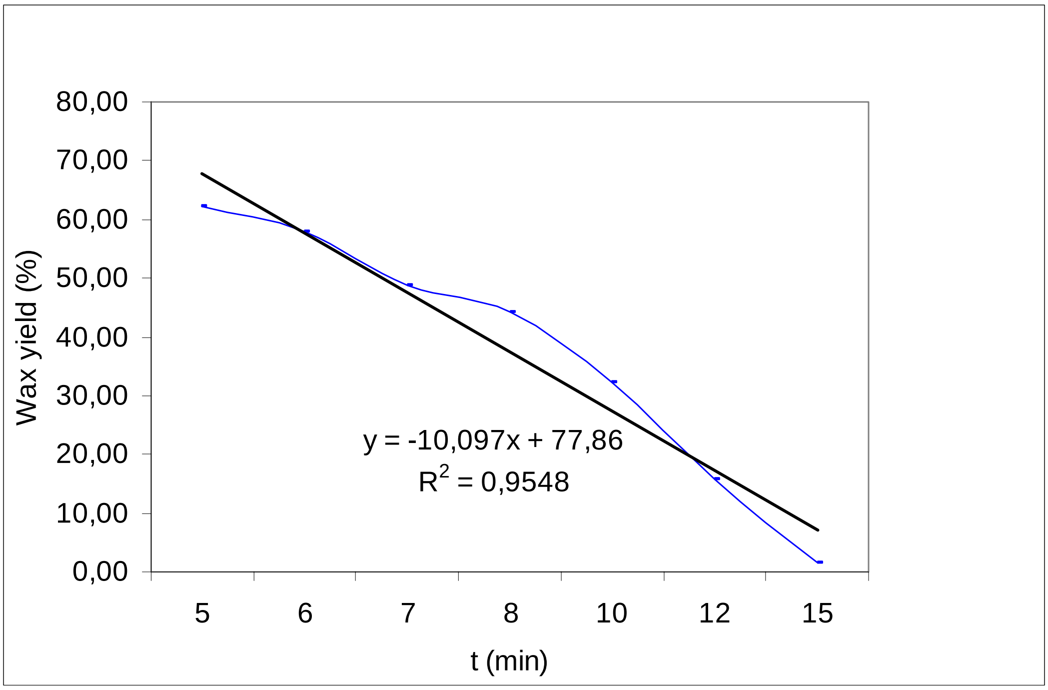

Figure D.9 Wax yield versus time of PE Wax at 480°C

APPENDIX E

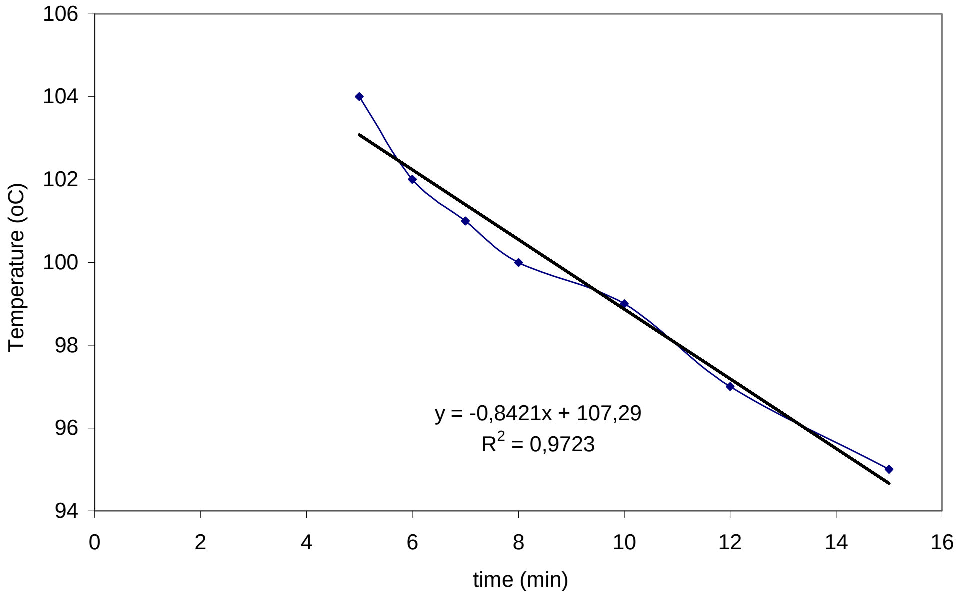

Figure E.1 Time versus temperature of PE Wax for congealing point at 440°C

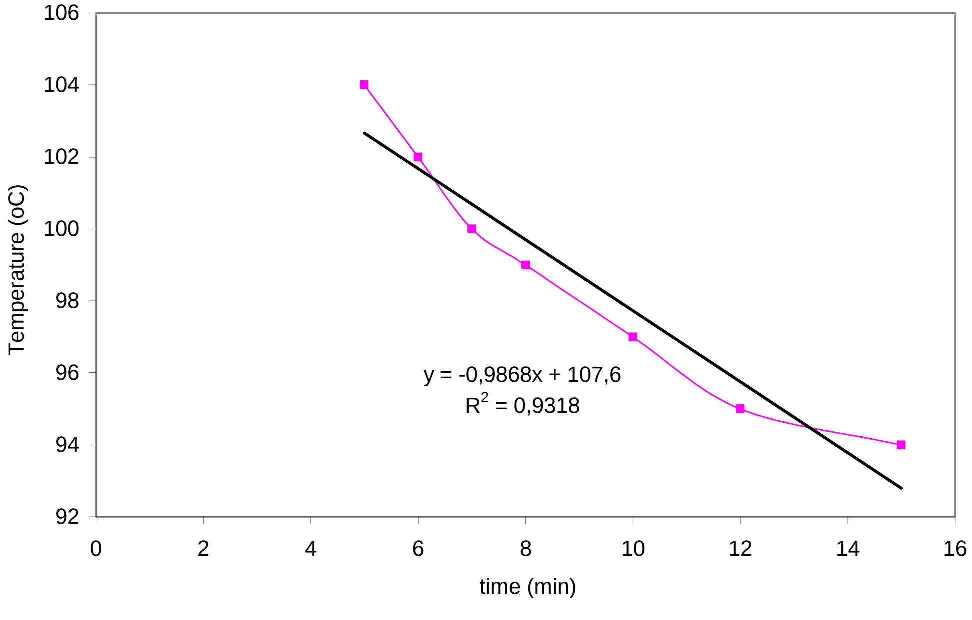

Figure E.2 Time versus temperature of PE Wax for congealing point at 445°C

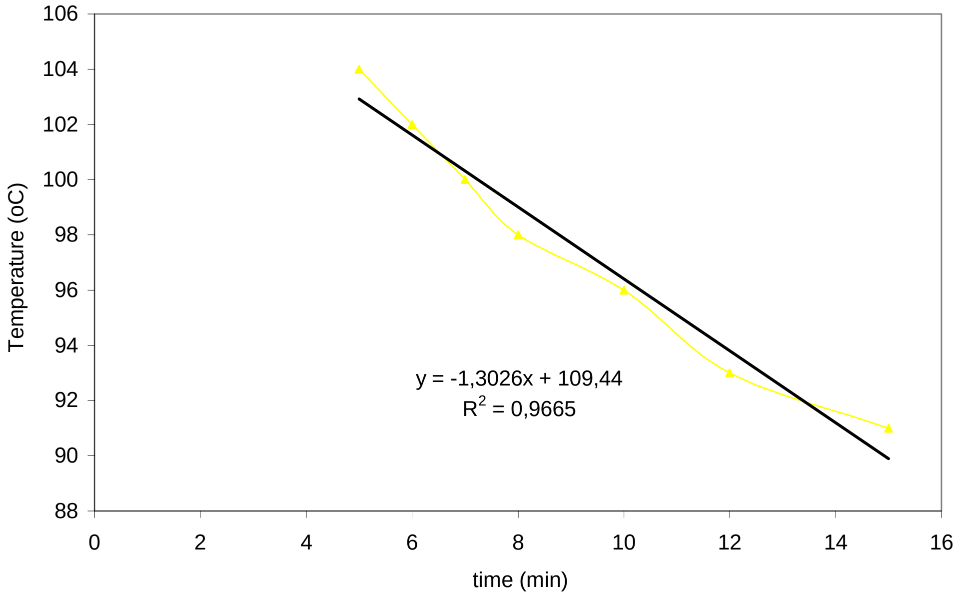

Figure E.3 Time versus temperature of PE Wax for congealing point at 450°C

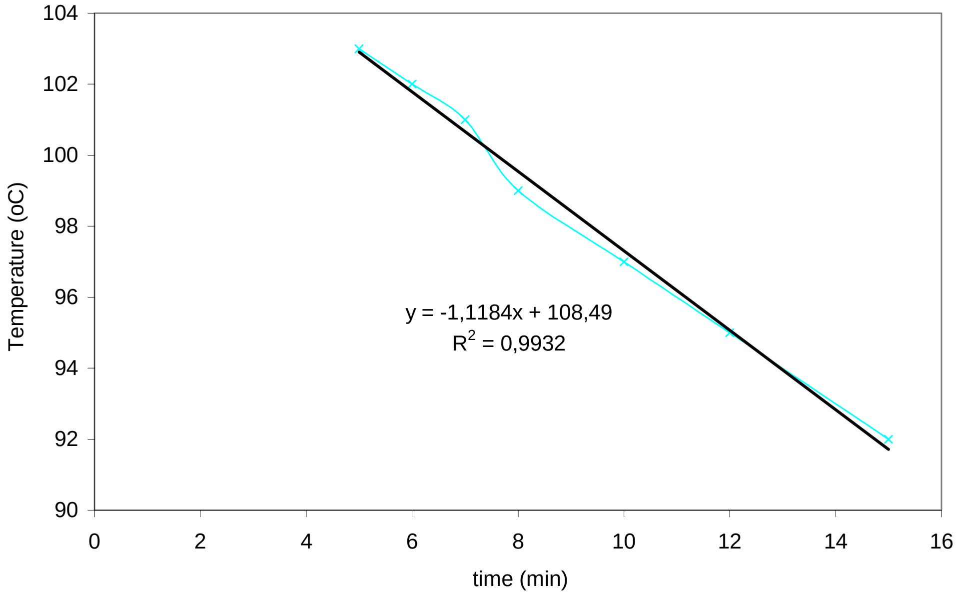

Figure E.4 Time versus temperature of PE Wax for congealing point at 455°C

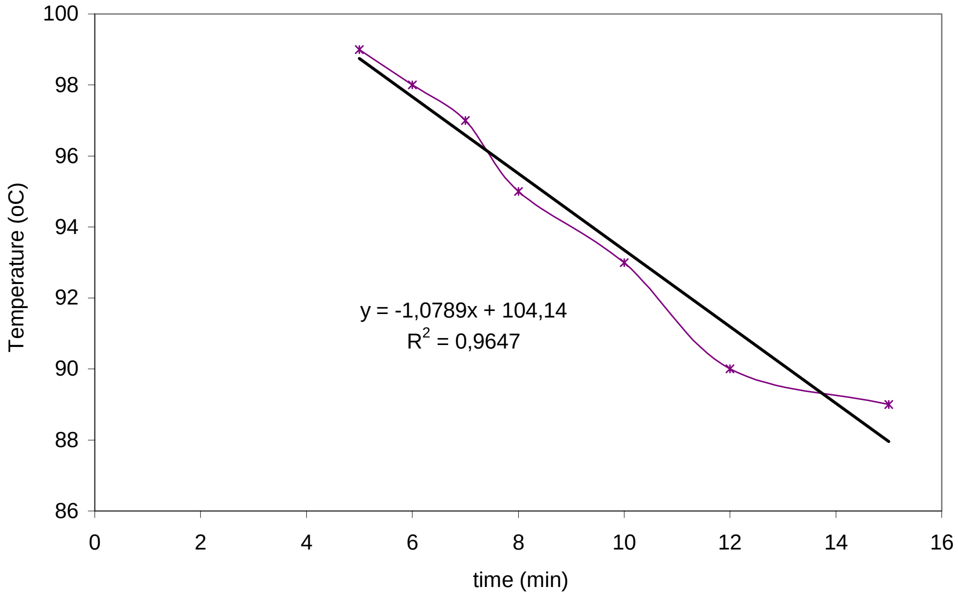

Figure E.5 Time versus temperature of PE Wax for congealing point at 460°C

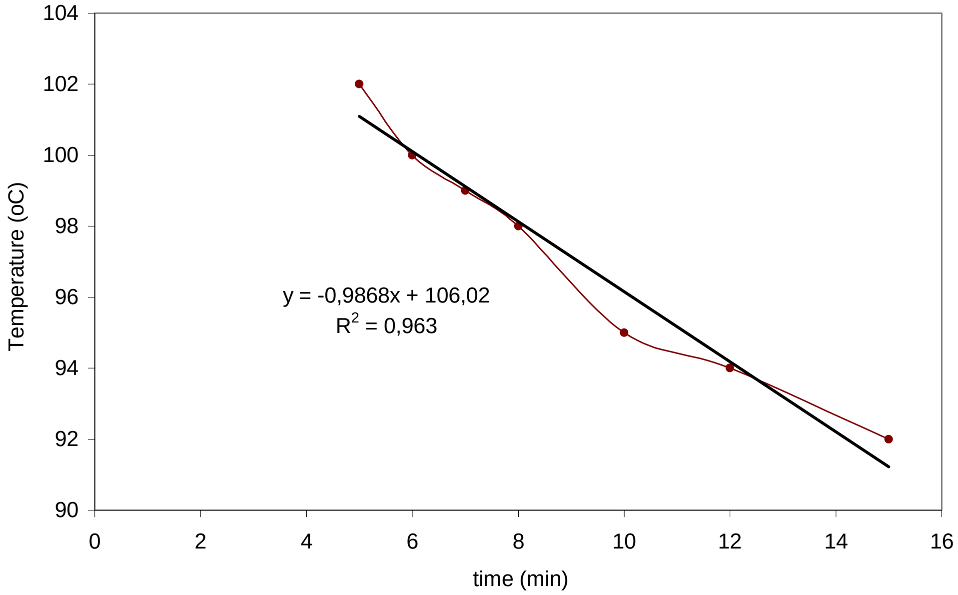

Figure E.6 Time versus temperature of PE Wax for congealing point at 465°C

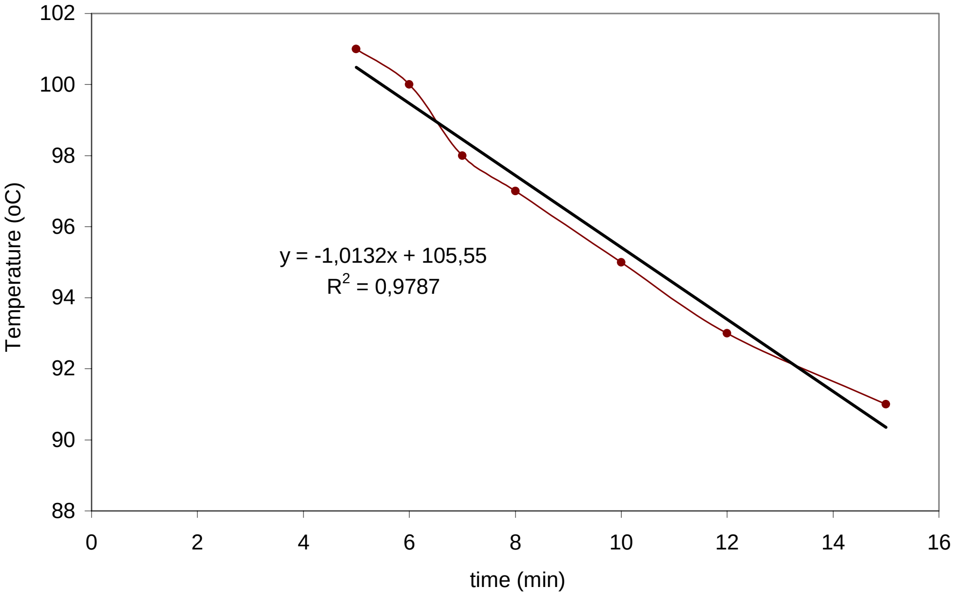

Figure E.7 Time versus temperature of PE Wax for congealing point at 470°C

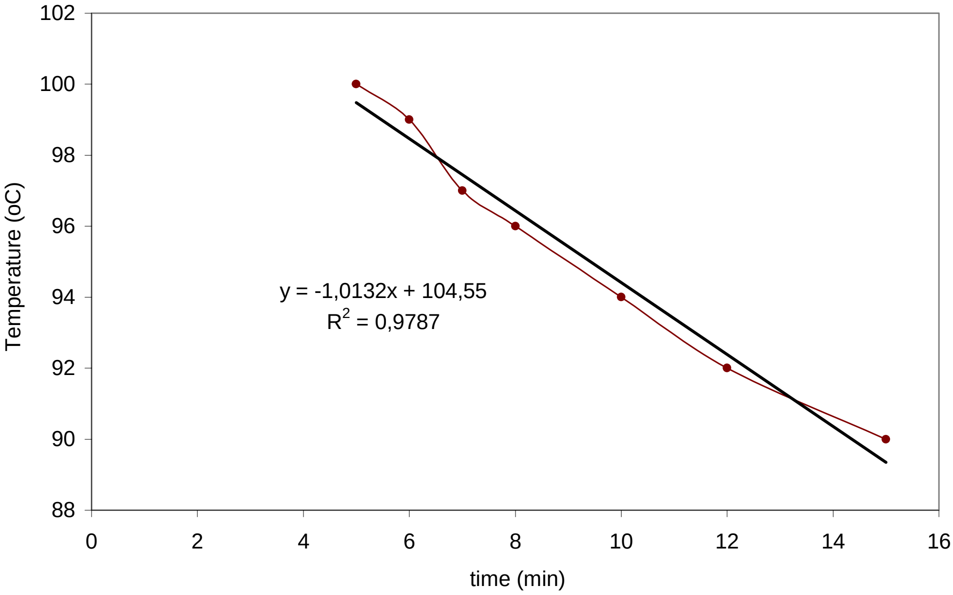

Figure E.8 Time versus temperature of PE Wax for congealing point at 475°C

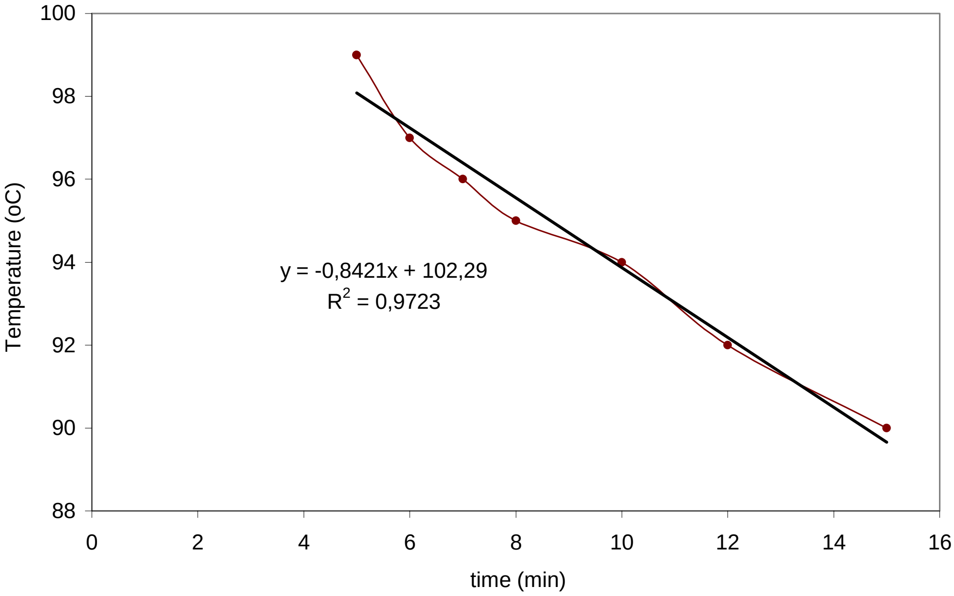

Figure E.9 Time versus temperature of PE Wax for congealing point at 480°C

APPENDIX F

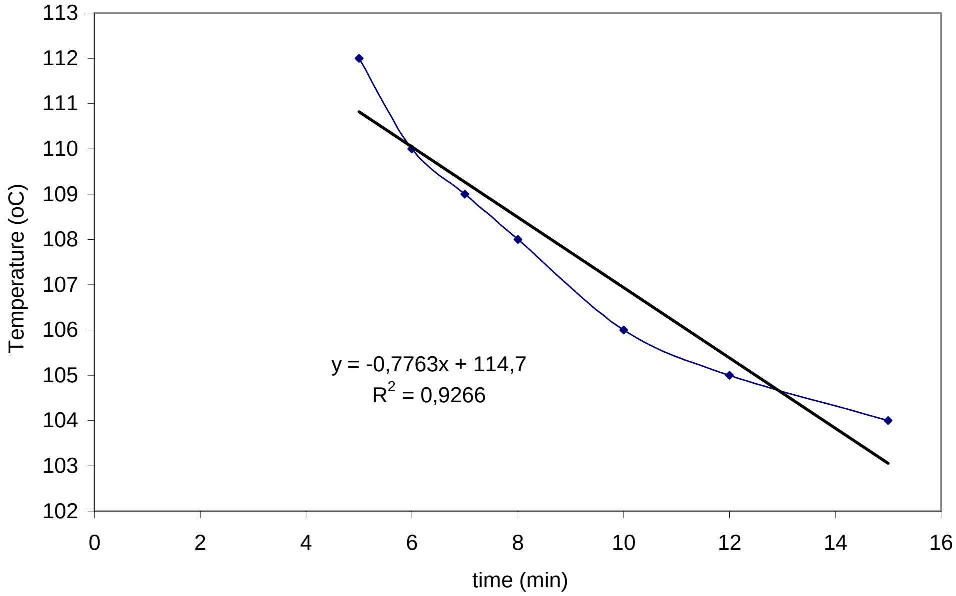

Figure F.1 Time versus temperature of PE Wax for drop melting point at 440°C

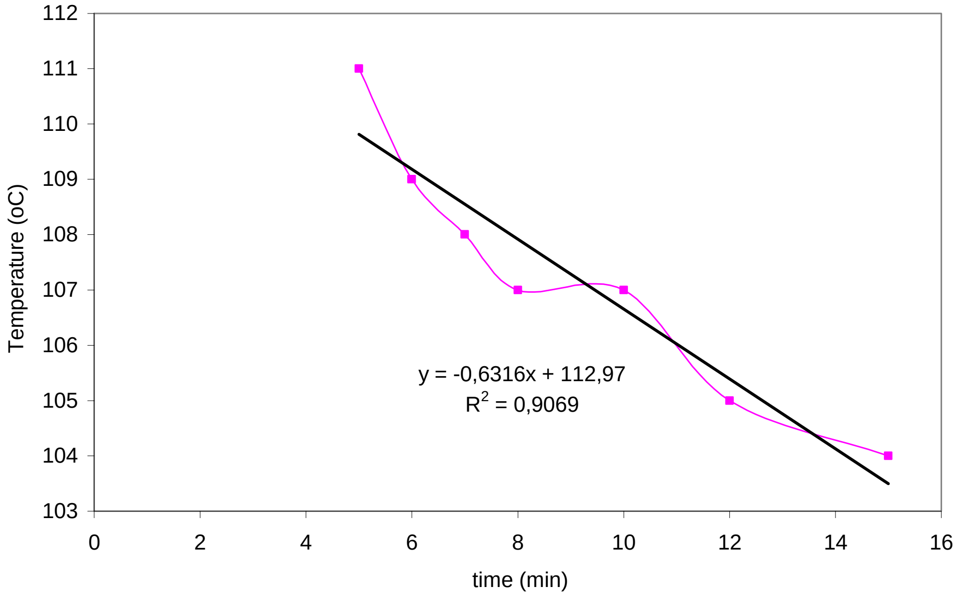

Figure F.2 Time versus temperature of PE Wax for drop melting point at 445°C

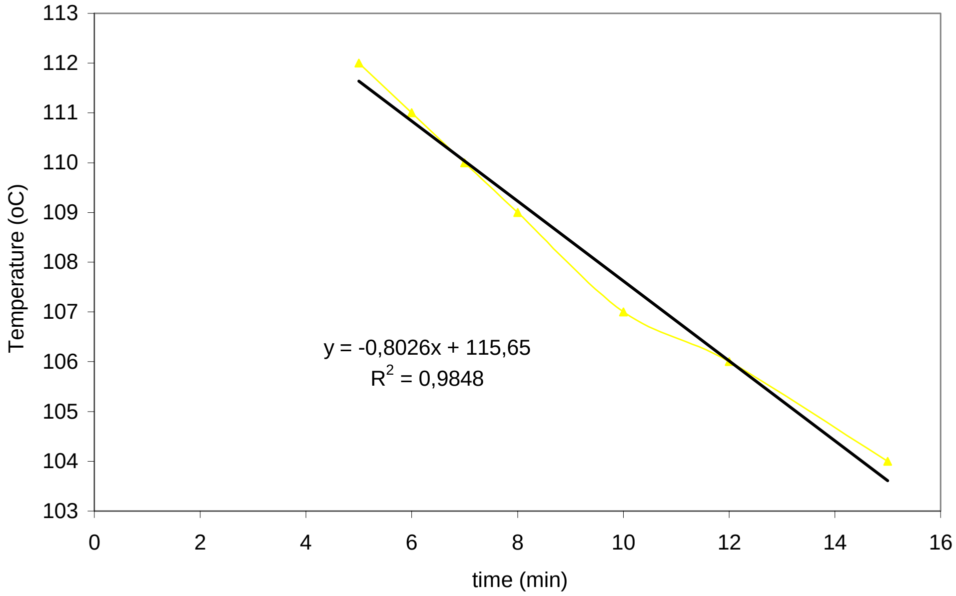

Figure F.3 Time versus temperature of PE Wax for drop melting point at 450°C

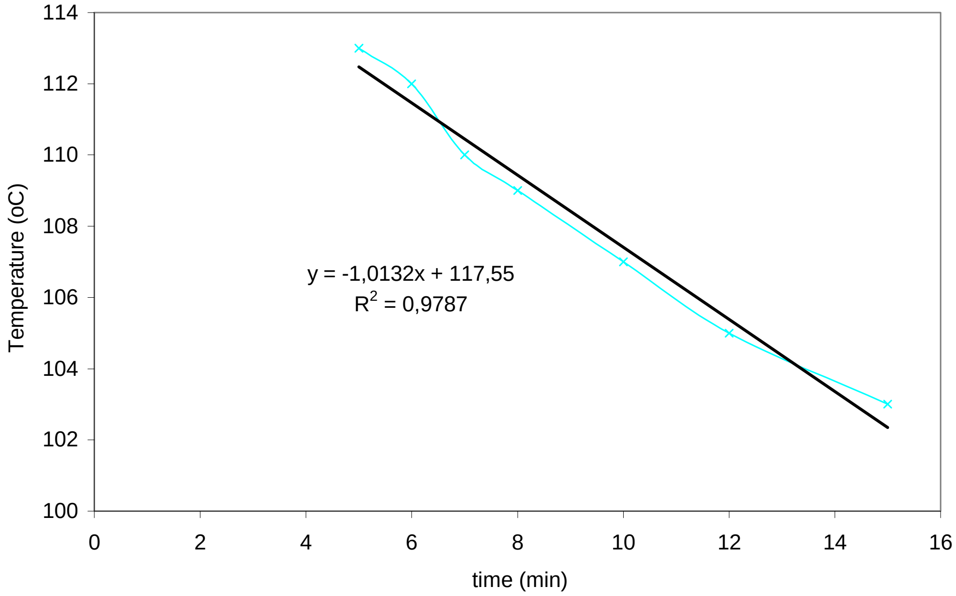

Figure F.4 Time versus temperature of PE Wax for drop melting point at 455°C

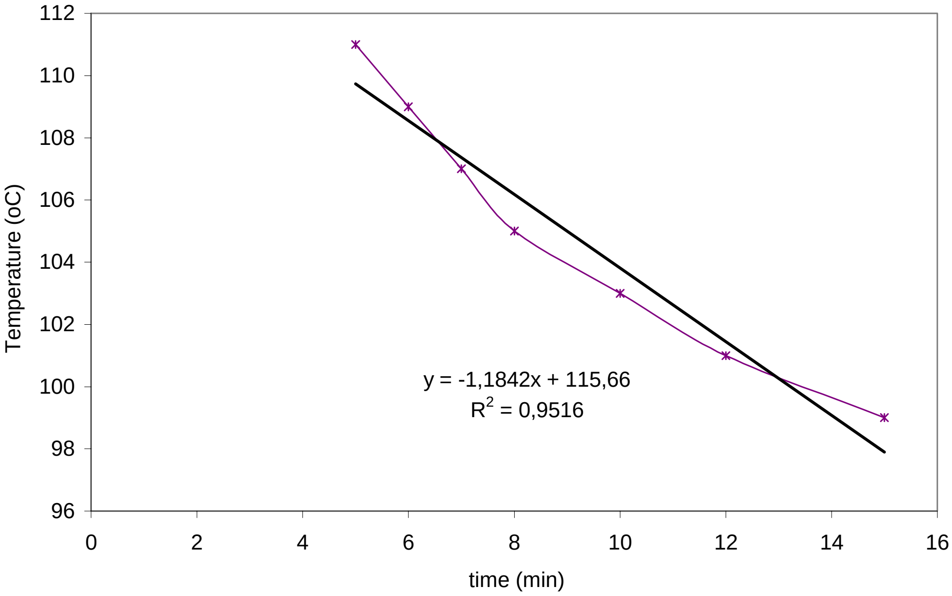

Figure F.5 Time versus temperature of PE Wax for drop melting point at 460°C

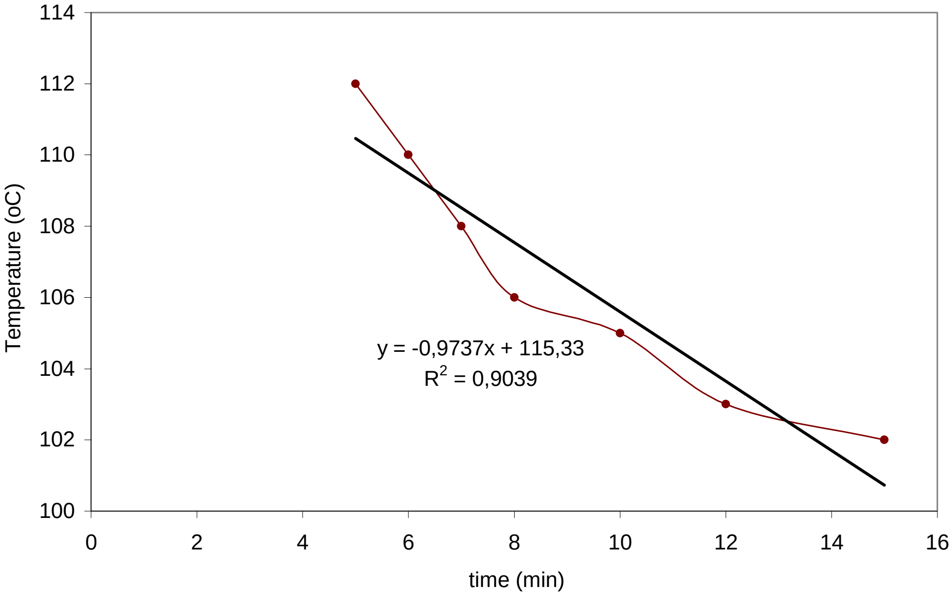

Figure F.6 Time versus temperature of PE Wax for drop melting point at 465°C

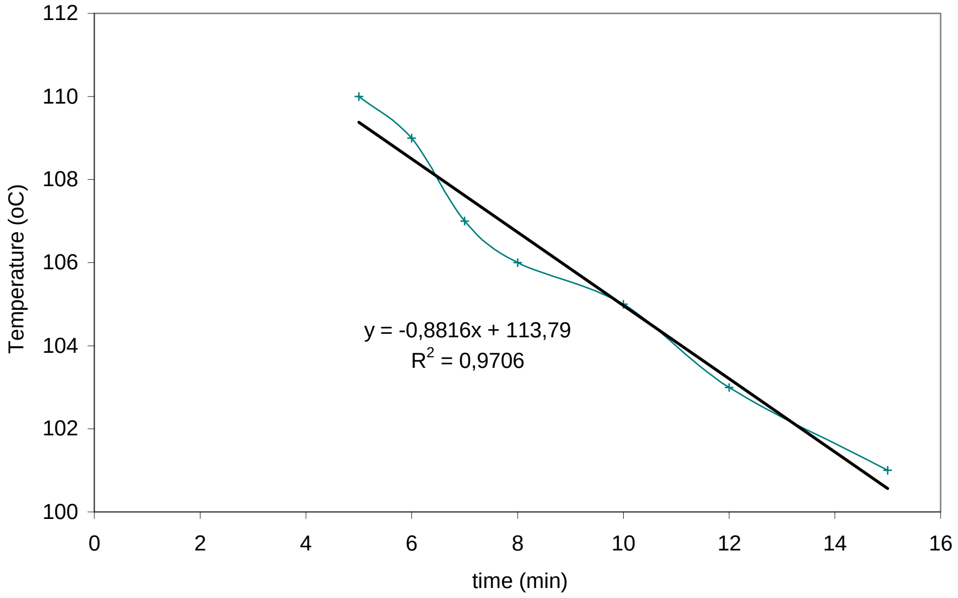

Figure F.7 Time versus temperature of PE Wax for drop melting point at 470°C

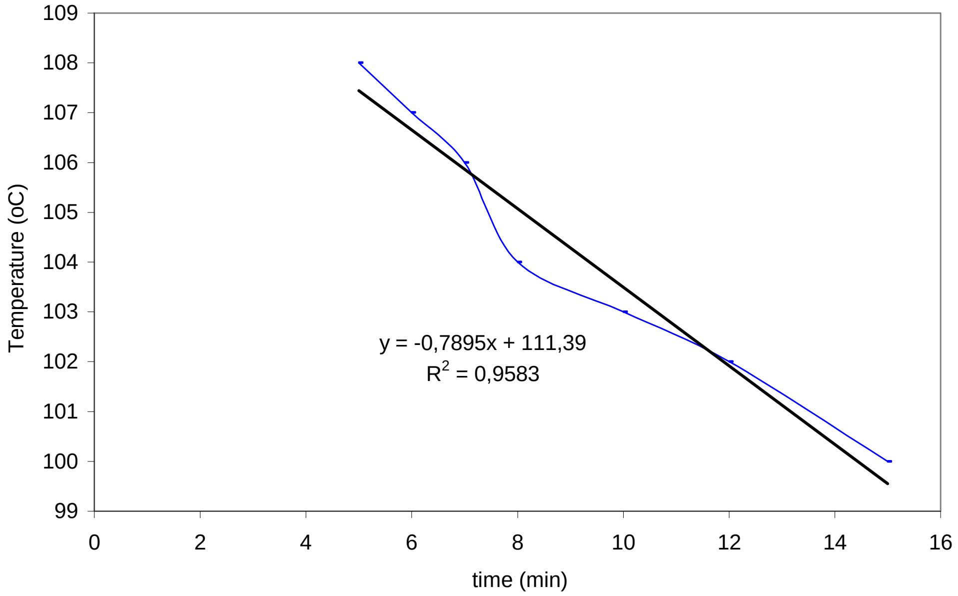

Figure F.8 Time versus temperature of PE Wax for drop melting point at 475°C

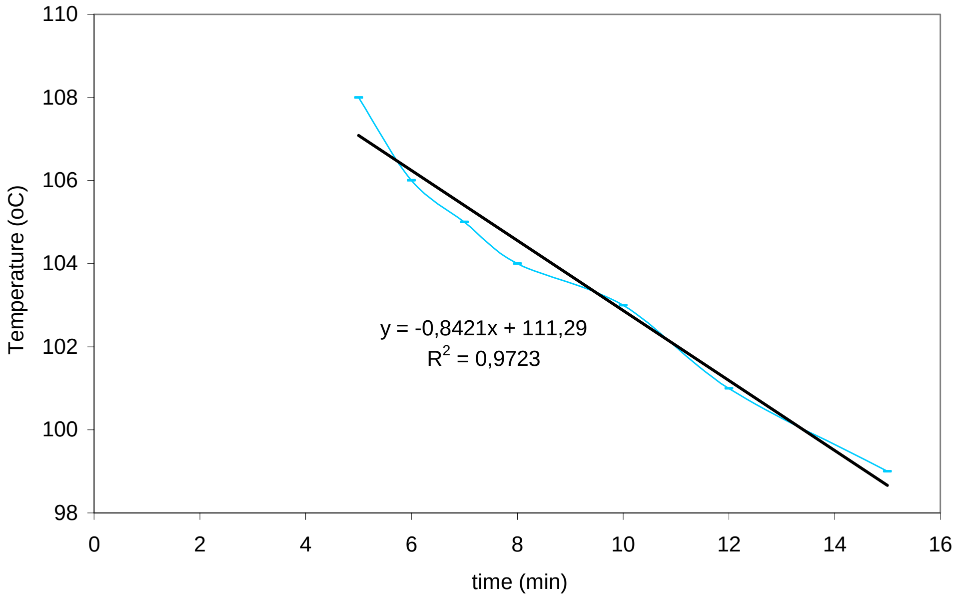

Figure F.9 Time versus temperature of PE Wax for drop melting point at 480°C

CURRICULUM VITAE

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2009-… İzmir Criminal Police Laboratory, Chemical Investigation Department Manager

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