PYROLYSIS OF POLYPROPYLENE BY ZIEGLER-NATTA CATALYSTS

Doctor thesis

Submitted to
Fachbereich Chemie
Universität Hamburg

In partial fulfilment of the requirements
for the German academic degree
Dr. rer. nat.

Ignacio Javier Núñez Zorriqueta

Hamburg, 2006

Gutachter/Reviewers:

Prof. Dr. W. Kaminsky

Prof. Dr. H. U. Moritz

Disputation: November 3th, 2006

A mi familia y Jasmin

Acknowledgments

This thesis was prepared between October 2003 and October 2006 at the Institute of Technical and Macromolecular Chemistry of the University of Hamburg.

First I would like to thank my professor, Prof. Dr. Walter Kaminsky, for the opportunity he gave me to work in his team and for the opportunity to work in a foreign country. For his support, for his advices and remarks and for the work environment he provided I am very grateful. I also want to thank him for his patience with my German.

This work also would not have been possible without the help of all group members. I would like to express my gratitude to my friends and colleagues Dr. Matthias Donner, Sascha Rulhoff and Dr. Björn Henninger for their help, advices and the friendship they offer to me. A special thanks also goes to my lab colleagues Dr. Katharina Wiemann, Burçak Arikan, Stefanie Derlin, Dr. Benjamin Hinrichs, Dr. Jens Kiesewetter, Dr. Christian Piel, Andreas Funck and Matthias Hoff for the friendly atmosphere in the lab and the fruitful discussions. I really appreciated to work and laugh with all of you. Many thanks also go to Tim Hölck and Ertac Tasci.

A special mention should be made for Ingrid Ruopp, Holger Stockhusen, Peter Harry, Jens Pagel, Angela Käther and Dörthe Hagemeister. Without their help it would not have been possible to carry out the experiments for this work.

Harald and Sigrid I would like to thank for being my “parents abroad”

Very special thanks are due to my parents for always supporting me and making my studies possible.

I also owe loads of thanks to Jasmin for always being there and supporting me when things had somehow gone wrong again.

CONTENTS

1. SUMMARY

Plastic's production and consumption increase day by day. All the plastics finish their useful life and have to be removed from the environment. The disposal of this plastic waste is an important target which could be approached by the feedstock recycling coming along with the recovery of raw materials.

The pyrolysis is a technical process known for years. It runs in an atmosphere without oxygen and at high temperatures. As a complementary recycling technology to combustion this technique is really attractive. But because of high temperatures required, in the economical point of view this process is still not viable for the pyrolysis of plastics. The use of catalytical systems and the complementation of the catalytic and the thermal degradation is one way to make this recycling technology more attractive for industry.

The current state of investigations is the use of fluid catalytic cracking (FCC) catalysts in pyrolysis reactions. But it would even be more economical if Ziegler-Natta-catalyst components, so far used as catalysts in the polymerisation reaction, could be used for the reverse reaction: the depolymerisation of polyolefins. In the present work the effects of the Ziegler-Natta catalysts compounds, such as titanium chlorides, on the pyrolysis of polypropylene were investigated.

Studies of the pyrolysis reaction of polypropylene have shown that at a temperature of 800 °C, mainly the monomer and another light hydrocarbon fractions can be recovered. When the temperature is decreased, heavy oil fractions increase (C9 fractions). But if the temperature is decreased to a certain minimum, the pyrolysis reaction can not run.

The Ziegler-Natta catalysts $TiCl_3$, $TiCl_4$ and $AlCl_3$ were now used for the pyrolysis reactions. Experiments conducted with different catalysts show that at

a temperature of 400 °C, the pyrolysis reaction can be carried out. The amount of PP pyrolysed was up to 90 wt %. The light oil fractions (C6 - C13) obtained were always the main components, varying in a range from 55 wt % (with 5 wt% of $TiCl_4$) to 81 wt % (with 1 wt % of $AlCl_3$).

It was possible to conduct experiments at lower temperatures as well. If the pyrolysis temperature was reduced to 250 °C ($AlCl_3$ and the combination of $TiCl_4$ and $AlCl_3$) the degradation was not successful - PP was largely not pyrolysed. But when reactions were run at 300 °C, valuable products were obtained. These reactions were carried out with $AlCl_3$ and the combination of $AlCl_3$ and $TiCl_4$. The minimum amount of catalysts needed was 1 wt% in respect of $AlCl_3$ and 5 wt % for the mixture of $TiCl_4$ and $AlCl_3$. Light oil fractions were the predominant fractions obtained with amounts between 20 and 65 wt%. The heavy oil fraction was important as well (10- 20 wt %). The gas fraction was not higher than 25 wt% (5 wt% of $TiCl_4$ and $AlCl_3$ in the ratio of 1:1).

The results of the conducted experiments have shown that the pyrolysis process temperature can be reduced to 300 ºC by using Ziegler-Natta-catalyst components. The decrease of the reaction temperature is tantamount to the lowering of costs. And the reduction in costs also makes the pyrolysis as a recycling technology attractive for industry.

For example, the combination of such recycling technology with the petroleum refinery process would make it possible to refine the pyrolysis products as gasoline and oil for the use in cars or for the heating industry.

2. ZUSAMMENFASSUNG

Die Herstellung als auch der Verbrauch von Plastikprodukten steigt Tag für Tag an. Irgenwann aber schließlich hat jedes Stück Plastik seinen Zweck erfüllt und muss entsorgt werden. Die Beseitigung dieser Kunststoffabfälle aus der Umwelt ist ein wichtiges Bestreben. Das Recycling stellt eine Möglichkeit dar, dieses Ziel zu erreichen und die Altkunststoffe wieder in Rohstoffe zurückzuführen.

Die Pyrolyse ist ein seit Jahren bekannter technischer Prozess, der bei hohen Temperaturen unter Ausschluss von Sauerstoff stattfindet. Neben der Verbrennung von Altkunststoffen ist dieses Recycling-Verfahren eine sinnvolle Technologie der Abfallverwertung. Wegen der hohen Reaktionstemperaturen, die für die Pyrolyse-Reaktion benötigt werden, war der Pyrolyseprozess unter wirtschaftlichen Gesichtspunkten für das Recycling von Plastik aber bisher nicht rentabel. Die katalytische Pyrolyse von Kunststoffen hingegen kann jedoch auch für die Industrie interessant sein.

Der Einsatz von fluid catalytic cracking (FCC)-Katalysatoren im Pyrolyseprozess wurde bereits erforscht, und es wurde aufgezeigt, dass bei Verwendung dieser Katalysatoren eine deutliche Temperatursenkung möglich ist. Es wäre indessen wirtschaftlicher, wenn die aus der Polymerisation bekannten Ziegler-Natta-Katalysatoren auch in der zur Polymerisation konträren thermischen Zersetzung von Kunststoffen einsetzbar wären.

Die vorliegende Arbeit befasst sich mit den Auswirkungen der Ziegler-Natta-Katalysatoren wie Titaniumchlorid auf die Pyrolyse von Polypropylen.

Vorangegangene Untersuchungen der Pyrolysereaktion von Polypropylen zeigten auf, dass bei einer Temperatur von 800 °C vorwiegend Monomere und andere leichte Kohlenwasserstofffraktionen gewonnen werden konnten. Bei niedrigerer Temperatur nahm hingegen der Anteil der Schwerölfraktionen (C9-

Fraktionen) zu. Wurde aber die Temperatur zu weit gesenkt, war die Pyrolyse von Polypropylen nicht mehr möglich.

Als Katalysatoren wurden nunmehr $TiCl_3$, $TiCl_4$ und $AlCl_3$ eingesetzt. Experimente mit den verschiedenen Katalysatoren zeigten, dass die Pyrolysereaktion auch bei einer Reaktionstemperatur von 400 °C abläuft. Polypropylen wurde bis zu 90 gew.% pyrolysiert, und die wichtigsten gewonnenen Komponenten waren die Leichtölfraktionen (C6 – C13) mit einer Spanne von 55 gew.% (mit 5 gew.% $TiCl_4$) bis zu 81 gew.% (mit 1 gew.% $AlCl_3$).

Es war sogar möglich, die Pyrolysereaktion bei niedrigeren Temperaturen ablaufen zu lassen. Aber bei einer Reaktionstemperatur von 250 °C (mit $AlCl_3$ und mit der Kombination von $TiCl_4$ und $AlCl_3$) war die Pyrolyse nicht mehr ausführbar – PP wurde zum größten Teil nicht zersetzt. Wurde hingegen bei einer Temperatur von 300 °C pyrolysiert, konnten wertvolle Sekundärrohstoffe gewonnen werden. Als Katalysatoren wurden hier $AlCl_3$ sowie die Kombination von $TiCl_4$ und $AlCl_3$ eingesetzt. Dabei war 1 gew.% im Hinblick auf den Katalysator $AlCl_3$ und 5 gew.% für das Gemisch von $TiCl_4$ und $AlCl_3$ die geringste Menge, die für die erfolgreiche Pyrolyse bei 300 °C notwendig war. Die größte Produktfraktion stellten die Leichtölfraktionen mit Ausbeuten von 20 gew.% bis zu 65 gew.% dar. Auch die Schwerölfraktion fiel mit 10 gew.% bis 20 gew.% ins Gewicht. Die Gasproduktion war mit 25 gew.% und weniger bei 5 gew.% $TiCl_4$ und $AlCl_3$ (in dem Verhältnis 1:1) vergleichsweise gering.

Die durchgeführten Experimente machen deutlich, dass die Pyrolysetemperatur unter Verwendung von Ziegler-Natta-Katalysatoren auf 300 °C gesenkt werden kann. Mit der Temperatursenkung geht eine Kostensenkung einher. Die Verringerung der Kosten macht die Pyrolyse als Recyclingmethode auch für die Industrie attraktiv.

Sinnvoll wäre es beispielsweise, die Recycling-Pyrolyse den Prozessen einer Raffinerie vorzulagern. Die Pyrolyseprodukte wie Benzin und Öle könnten sodann veredelt und als Kraft- oder Heizstoffe verwendet werden.

3. INTRODUCTION

3.1. Polymers Plastics, uses and possibilities

Polymer is a term used to describe a long molecule consisting of structural units and repeating units connected by covalent chemical bonds. The term is derived from the Greek words: polys meaning many, and meros meaning parts. The key feature that distinguishes polymers from other molecules is the repetition of many identical, similar, or complementary molecular subunits in these chains. These subunits, the monomers, are small molecules of low to moderate molecular weight, and are linked to each other during a chemical reaction called polymerization.

Instead of being identical, similar monomers can have varying chemical substituents. The differences between monomers can affect properties such as solubility, flexibility, and strength. Most polymers are organic, with carbon-based monomers, there are also inorganic polymers; for example, the silicones, with a backbone of alternating silicon and oxygen atoms.

The term plastic describes a wide range of materials and compounds made from different polymers. Many polymers are malleable and have the property of plasticity. The term plastic derives from this property. Plastics can be formed into objects or films or fibres and are designed with immense variation in properties such as heat tolerance, hardness, resiliency and many others. Combined with this adaptability, the general uniformity of composition and light weight ensures their use in almost all industrial segments.

There are two main types of plastics; thermoplastics, (more than 80 %) which physical behaviour depends on the external temperature. They are soft when heated and becomes harder by cooling. Most common thermoplastics are HD-PE for detergents bottles, LD-PE for flexible containers, PP used in automotive

parts, PET used in bottles, PVC for pipes etc. The other main type are the thermosets plastics. They are hardened by a curing process and can not be remelted or re-moulded. Different examples of thermosets plastics are PU, epoxy and phenolics.

As the physical and chemical properties of individual polymers can differ depending on the end-use applications, HD-PE for example is resistant to impact, electricity and chemicals. PP can be “hot filled” and has a good tensile strength. As well it can be used in fibres and filaments due to the possibility to be extruded. PET, however, has good gas barrier characteristics and therefore is suitable for packaging carbonated drinks, and PVC has good insulation properties.

The chemical process to produce a polymer is called polymerisation. It is the process of joining together a large number of small molecules, monomers, to make a smaller number of very large molecules. This polymerisation process can occur by two different mechanisms: by addition polymerisation and condensation polymerisation.

The addition polymerisation is the joining together of two or more monomers units ($M + P_n \xrightarrow{k_n} P_{n+1}$). Free radical polymerisation (divided into three separate processes: Initiation of the chain reaction, propagation and termination) and living polymerisation (it does not undergo a termination reaction and continues until the monomer supply has been exhausted) are the kind of addition polymerisation.

The polymers formed by addition polymerisation are thermoplastics. These include PE, PP and PS.

The condensation process ($P_n + P_m \xrightarrow{k_{nm}} Pn+m$) is a polymerisation process that involves a chemical reaction between multifunctional monomer molecules. In a condensation polymerisation reaction (also called step-growth polymerisation), two multifunctional monomer molecules react together to form a dimer (two molecules joined together), which can in turn react with other

monomer and dimer molecules, etc., until a long polymer is formed. A multifunctional monomer is a molecule that has more than one potential reactive site by which it can form intermolecular chemical bonds. In a condensation polymerisation each bond-forming reaction generates a small molecule by product like a molecule of water.

This condensation process can produce both thermoplastics and thermosetting plastics. For example polyesters and nylon are formed by this process.

3.2. Recycling, processing and statistics

The production (Fig. 3.1) and the consumption of plastics has dramatically grown within the last years, reflecting changes in the manufacture and use of plastics. With regard to the consumption of plastics in western Europe from 1991 to 2003, figure 3.2 indicates an increasing average of 3 % per year [1].

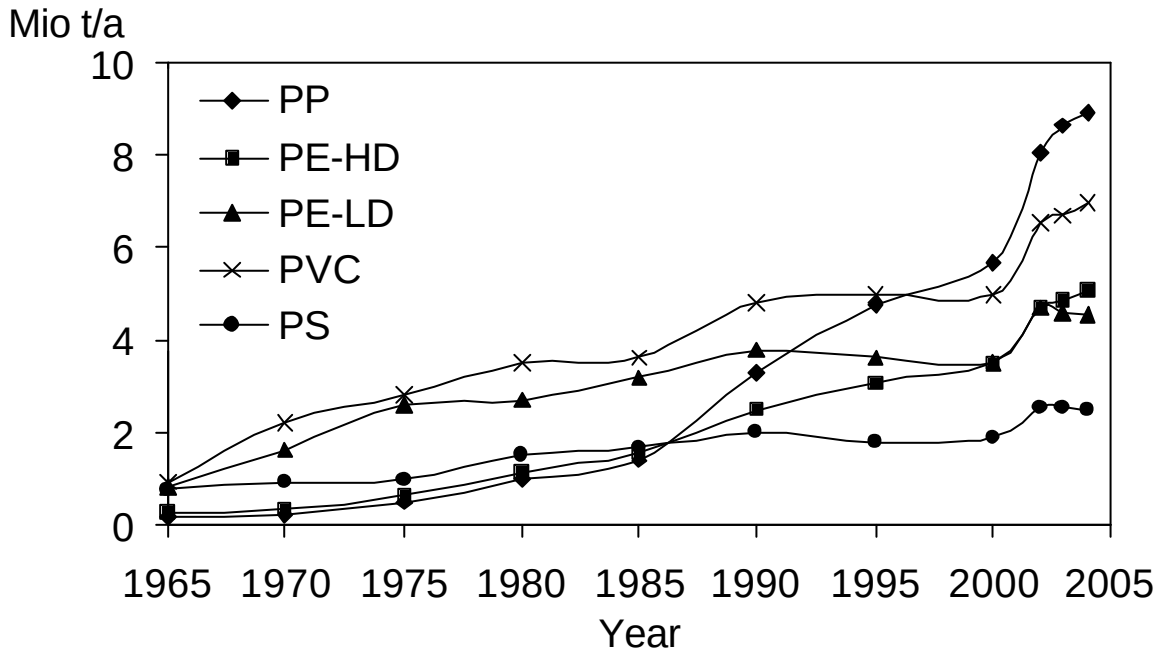


Figure 3.1.- Polymer production in western Europe (APME 2004 annual report)

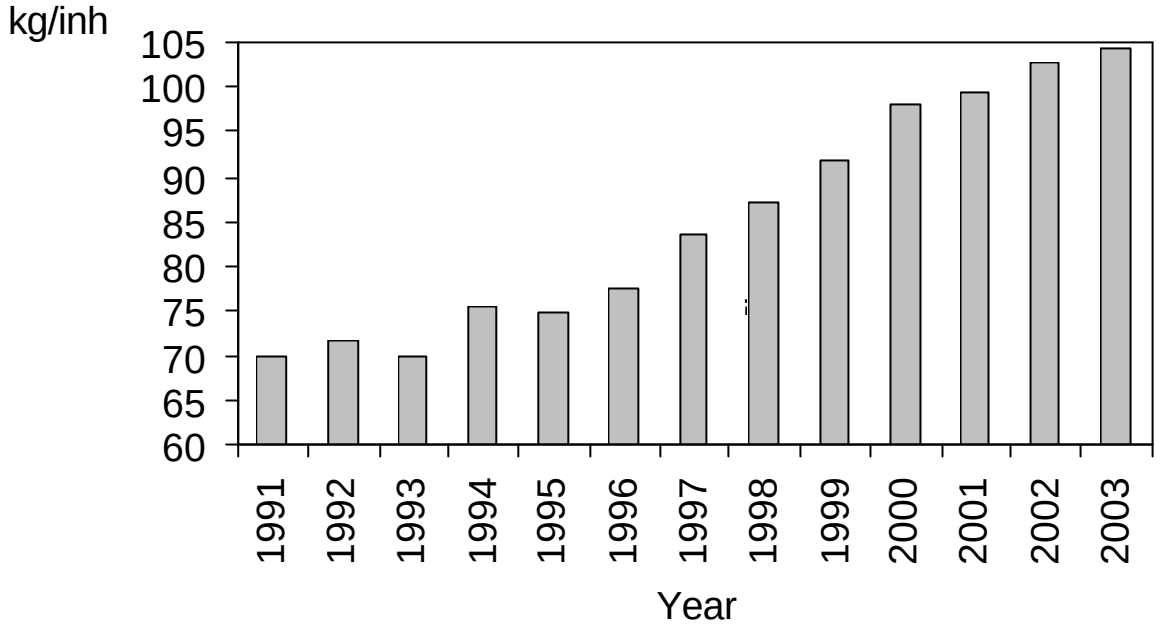


Figure 3.2.- Consumption per capita of plastics in western Europe

In Western Europe, two third of the total waste generated (figure 3.3) is municipal solid waste (MSW) of which 8 wt% are plastics (corresponding to 20 volume percent). The second stream in importance comes from the distribution and industrial sectors with 10,5 kg/inh/year. Local and regional authorities, are confronted with a number of environmental, economic and social issues concerning the solid waste in general and the plastic waste in particular. These issues include the saturation of traditional waste disposal facilities, the public demand for selective material collection services, the visual pollution and the legal obligations to comply with legislative targets. Constraining factors in landfilling plastics concern the volume of space that they occupy in relation to their weight. In densely populated regions incineration is practically a necessity.

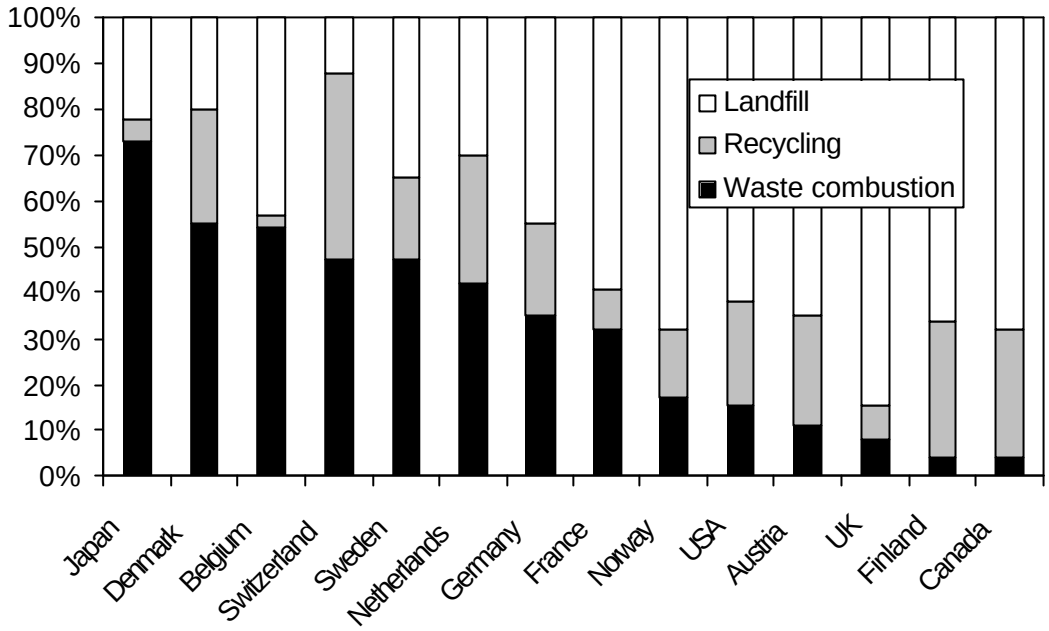


Figure 3.3.- Waste disposal in different countries in 2003.

To reduce the environmental impacts of growing waste streams, the European legislature has introduced a number of obligations on certain waste products, which must be respected by all the member states. The E.U. waste management policy focuses on waste hierarchy, giving priority to waste prevention or reduction followed by re-use, recycling, recovery and residual management. Such a strategy includes an integrated approach to waste management with emphasis on material recycling that is preferred over energy recovery.

Waste prevention (or reduction) involves alterations in product design as well in consumer habits. Such strategies assure that the two objectives of less waste produced and less hazardous constituents utilized in production are both met. Waste prevention is a strategy that prevents waste and its associated risk from being produced in the first place.

The term feedstock recycling indicates a family of chemical processes that turn waste plastic back into petrochemical feedstock, usually liquids or gases, but sometimes solid or waxes that can be used again as raw materials in the production of new petrochemicals and plastics without any deterioration in their

quality and without any restriction regarding their application. These processes constitute a remarkable technological improvement in the plastic recycling technologies since they can treat heterogeneous and contaminated plastics without problems with a limited use of pre-treatments. Mixtures of plastics can be used without problems as long as the halogen content of the refuse does not exceed certain critical values [2]. The purpose of feedstock recycling is to break down the collected waste plastics into their basic chemical components and to use them as secondary raw materials in the petrochemical industry, steelworks and refineries. Unfortunately, petrochemical plants have much greater capacity than plastics manufacturing plants (6 to 10 times more) and they are greatly less efficient when size decreases (economical and environmental point of view).

The necessity to use existing petrochemical plants implies that plastic waste stream can be fed together with the usual feedstock only if they meet some severe input specifications:

- Oil: It must be pumpable and sprayable (for certain processes)
- Solid: It must have free-flow properties
- Chlorine content: It must be strictly limited (Corrosion problems)
- Heavy metal content: It must be severely restricted (Interferences with catalytic processes)
- Larger inorganic particles: They must be limited due to the fact they can settle fast blocking the lines and pumps

3.3. Ziegler-Natta catalyst

The terms Ziegler catalysts and Ziegler – Natta catalysts are used to denote the general range of catalyst systems formed from the following building blocks:

- An organometallic compound of a metal of groups 1, 2, or 13 (e.g., an aluminum trialkyl)
- A compound of a transition metal from groups 4 – 8 (e.g., titanium tetrachloride)

These two components are mixed in an inert solvent and form polynuclear complexes. It is assumed that unsaturated molecules such as ethylene are bound to the coordination site and then inserted into the metal – ethyl bond. This insertion produces another vacant coordination site, and the process can begin again. If this chain mechanism is broken, oligomers are formed, but if the insertion reaction is repeated indefinitely, long-chain polymers are obtained.

The most important application of Ziegler catalysts is the synthesis of polyolefins [3-8].

The first oligomerisation with a Ziegler catalyst system was discovered in 1952 by HOLZKAMP at the Max Planck *Institut für Kohlenforschung* [9, 10]. A growth reaction with aluminum alkyls and ethylene was carried out with addition of nickel salts. The Ni – Al catalyst system led to exclusive formation of ethylene dimers (i.e., butenes) instead of a broad distribution of α-olefins. This "nickel effect" marked the birth of the Ziegler catalysts.

In 1953 Karl Ziegler developed the catalytic polymerisation of ethylene [11]. Gaseous ethylene was polymerised quickly to high-molecular polymers at pressures of 100, 20 or 5 atm and even at atmosphere pressure using simple producible catalysts. With this discovery [12-14], based on fundamental investigations of the reaction between ethylene and organometallic compounds, especially aluminum compounds, Ziegler has changed the world in a twofold way: He initiated many scientific studies in the field of catalysis using organometallic compounds and his discovery was of outstanding relevance for the industrial synthesis of polyolefins. The production of polyethylene by polymerisation of ethylene under normal pressure or pressures up to 5 MPa and moderate high temperatures (up to 90 °C) using organometallic catalysts formed by mixing alkyl aluminum compounds and transition-metal chlorides,

such as $TiCl_4$ in a hydrocarbon diluent (diesel oil or petrol) was transferred into an industrial process within a few months [15]. With these catalysts Natta and co-workers polymerised propylene to isotactic polypropylene. They discovered the principles of the regio- and stereospecific polymerisation of 1-alkenes [16, 17]. The process to synthesize isotactic polypropylene was again transferred into an industrial process within a few years because a polymer with new properties was accessible [15]. These catalysts can also be used for the copolymerisation of ethylene and propylene to produce ethylene–propylene elastomers; again these were new polymers [18].

A further important development in olefin polymerisation catalysts was the use of metallocenes activated by methylaluminoxane (MAO) [19-23]. These catalyst systems were discovered in the 1970s by Kaminsky and Sinn at the University of Hamburg, and very soon extremely high activities (e.g., 40 000 kg polyethylene per gram metal per hour) were being observed. Catalysts based on metallocene/MAO led to a new breakthrough in the synthesis of polypropylene in 1985. The use of bridged bis(indenyl)zirconocenes, developed by BRINTZINGER at the University of Constance, enabled isotactic polypropylene to be produced with extremely high catalyst activities and stereoselectivities.

3.4. Pyrolysis

Thermolysis is a thermal decomposition process of (waste) products involving partial vacuum and oxygen free environment. The feedstock is heated (in the absence or presence of water) for a short time. The different thermo-chemical processes are combustion, gasification, pyrolysis and hydrothermal liquefaction.

Combustion is a sequence of chemical reactions between a fuel and an oxidant accompanied by the production of heat or both heat and light. (In a complete combustion reaction, a compound reacts with an oxidizing element.

The products are compounds of each element in the fuel with the oxidizing element.) (sollte vielleicht weg)

Pyrolysis is the thermally initiated decomposition of organic material by heating in the absence of oxygen. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C (up to 800°C). The organic materials are transformed into gases, small quantities of liquid, and a solid residue containing carbon and ash.

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, petroleum coke or biomass, into carbon monoxide and hydrogen.
The processes are carried out in a controlled oxidative atmosphere.

Hydrogenation is a called a chemical reaction between molecular hydrogen and an element or compound, ordinarily in the presence of a catalyst. The reaction may be one in which hydrogen simply adds to a double or triple bond connecting two atoms in the structure of the molecule or one in which the addition of hydrogen results in dissociation of the molecule (called hydrogenolysis, or destructive hydrogenation).

By the use of heat the bonds in the backbone of a polymer are cleaved.

The present work is focused in the pyrolysis process, a promising process from the technological and economical point of view [24, 25]. Mainly, this is a consequence of the potential high value-added of the final products and the high electrical conversion efficiency proper of the technologies that could be adopted downstream.

Some general advantages of pyrolysis are:

- It operates without the need of air or the addition of hydrogen and doesn't involve elevated pressures.

- It can convert waste plastics, which can not be efficiently recycled by alternative means, into higher valued products.
- The gas release is 5 to 20 times lower than the gas release of a combustion.
- Pollutants and contaminants become concentrated in a coke-like matrix, which is a solid residue of the process [26].

3.4.1. Pyrolysis reactors

The reactors used in pyrolysis processes are fluidized beds, melting pots, autoclaves, tubular reactors and rotary kilns.

3.4.1.1. Fluidized bed

The University of Hamburg has investigated the suitability of plastic wastes after the first oil crisis in 1975 [27, 28]. For cracking plastics into oil the low heat transfer and the high heating energy needed as well as the different impurities such as inorganic fillers were problematic. One possibility to solve all those problems was the installation of a process that was able to use filled and dirty plastics in a fast pyrolysis process [29-35]. In the years from 1973 to 2005, different fluidized bed reactors were built at the institute for technical and macromolecular chemistry, continuously working with plastics throughput of 50 g/h (LWS-1), 500 g/h (LWS-2), 2 kg/h (LWS-3, LWS-4), 3 kg/h (LWS-5), a small pilot plant of 30 kg/h (TWS-1) (figure 3.4) for plastics and a pilot plant of 200 kg/h for whole tires (TWS-2) [36, 37]. The plastics are fed into the reactor through a double flap screw. The fluidized bed consists of quartz sand and the reactor working temperatures are between 300 to 900 ºC. The fluidizer agent can be pyrolysis gas or a nitrogen stream preheated. The heat input takes place through fire pipes heated by pyrolysis or propane gas. The exhaust gases are redirected to a heat exchanger. The product gases are separated from residual

carbon and fine dust in a cyclone. The gas flow is then directed through two packed condensation columns. Condensed oil fractions are distilled (fractions boiling from 135 to 145 ºC) in two columns. Also tar, with a high boiling point range, is produced as well as two fractions, toluene and benzene. The gases mostly stripped off liquid products, pass to an electrostatic precipitator where small droplets are removed. Subsequently, the gases are compressed in five membrane compressors connected in parallel and stored in 3 gas tanks. Part of the gases serve as fuel for the heating system and the remainder is used for fluidizing the sand bed. The excess gas is flared.

The Hamburg process can be varied in some parameters such as pyrolysis temperature, type of fluidizing gas and residence time. This process has been used as well for oil and gas recovery from oil shale, oil sand and biomass (wood, lignin, bark, oil seed and fat) [38-40].

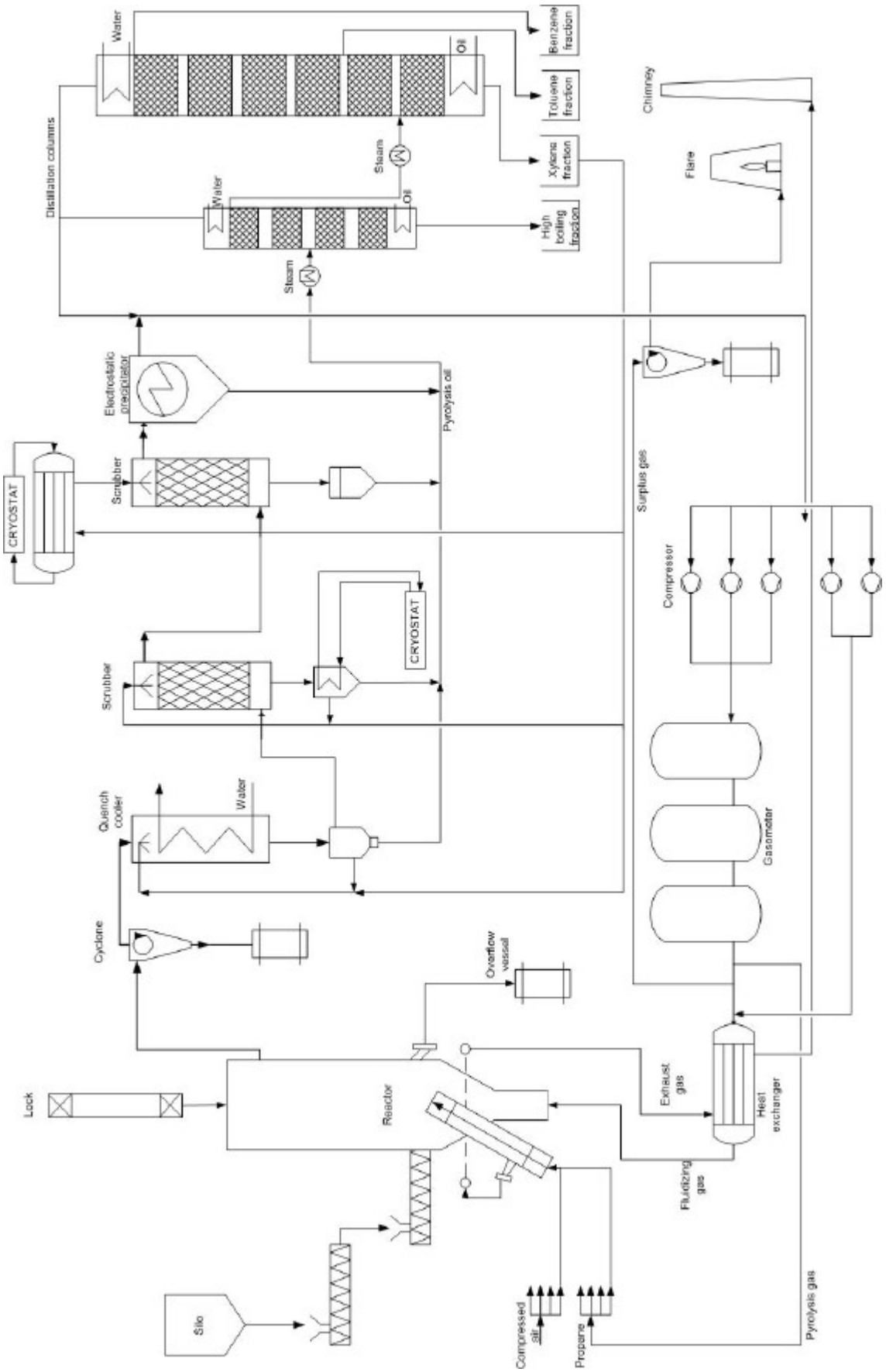


Figure 3.4.- TWS pilot plant Flow char of the Hamburg pyrolysis process.

BP chemicals has investigated the conversion of waste plastics into petrochemicals [41]. The “Polymer cracking process” was first tested on a lab scale and later on a continuous pilot scale (400 t/y) at the BP’s Grangemouth site in UK.

Prepared mixed waste plastics, oxygen free and with a maximum of 5% of non-polymeric impurities, are introduced into a bubbling fluidized bed reactor where the low temperature cracking takes place. The fluidized agent are nitrogen and recycled gas that fluidises the sand. Once the plastic is introduced into the reactor the pyrolysis reaction starts obtaining gases that leave the reactor with the fluidizing gas [42-45]. The gaseous products are purified from residual carbon and fine dust first in a cyclone, and then in a successive guard bed which catches the chloride content, coming from PVC destruction, by the reaction of CaO with HCl. The main result is $CaO/CaCl_2$ that has to be landfilled. An intermittent withdrawal of material from both fluidized bed reactor and guard bed is necessary to purge the bed from accumulate unwanted materials.

The gas resulting from the process is collected in a two-stage process. A venturi loop system partially condenses the gas turning it to a waxy hydrocarbon product. The not condensed gas stream is compressed, reheated and returned to the cracking reactor as fluidizing gas. Excess gas is continuously removed to keep the process operating at a pressure of 4 bar and partially used as fuel for indirect heating of the fluidized reactor [25, 42, 46]. The Polymer Cracking Process has an efficiency of approximately 80 % conversion of plastic waste to petrochemical products with an additional 10 – 15 % used as fuel gas in the process itself. The obtained hydrocarbon feedstock is a high quality hydrocarbon while the waxy product can be used as feedstock material for steam crackers or can be fed into refinery units (FCC unit).

Advantages and disadvantages

The most important variable in a pyrolysis process is the temperature. Depending on it and on the type of plastic different products will be obtained.

For example, low temperature processes generally enhance liquid products whereas higher temperatures generate gas. Some polymers such as polystyrene and polymethylmethacrylate give high monomer yields, approaching 100 % when pyrolysed, while polypropylene yields only about 2 % of its weight [22, 47].

As mentioned before, another variables in this process are residence time, reactor type, feeding arrangement and condensation arrangement.

The fluidization technology allows to exalt the potential benefits of a pyrolysis process [48]. Different advantages can be listed for fluidised bed reactors utilised for thermal treatments of waste [49].

- Fast and good mixing of solids. Uniform temperature conditions throughout the fluidized bed.
- The well-mixed solids permit to keep constant the temperature resisting fast temperature changes and avoiding the formation of cold or hot spots. Constant process temperature gives uniform products and allow short residence time at moderate temperatures.
- The operating range of temperature is lower than that of other reactors.
- High heat and mass transfers between gas and particles.
- The liquid-like flow of particles allows continuous controlled operations with easy handling. The circulation of solids between two fluidized beds makes possible to remove or add the high quantities of heat produced or needed in large reactors as well as to substitute part of the sticky or agglomerated bed material with fresh solids.
- High process flexibility. Use of different fluidizing agents, operating temperatures and gas residence times, as well as the operation with or without catalysts.
- Lower maintenance cost, consequence of the absence of moving parts.

The main disadvantages are,

- Friable solids, bed materials, catalysts are pulverized and may be carried along with the gas.
- Agglomeration and sintering of fine particles, therefore. The process conditions can change, the temperature will be not constant in the whole reactor. The fluidised material has to be changed.
- The residence times are not uniform because of the fast solid mixing.
- Erosion of pipes and vessels by abrasion of bed particles.
- Difficult scale-up.

3.4.1.2. Rotary kiln

The rotary kiln with corresponding post-combustion chamber is the classical universal unit common in pyrolysis process for plastic wastes, rubber and scrap tires. The rotary-kiln reactor has a long, refractory-lined, slightly inclined cylindrical tube through which waste is moved continuously. Because of the very poor heat exchange the installation of a long cylinder kiln is a necessity. In the first section, the waste is dried. In the second section, the dried refuse is moved onto a rocking grate where it is partially pyrolysed. The third and last section is a cylinder where pyrolysis is completed. The cinders spill out at the end of the cylinder. A tall flue gas stack, fan, or steam jet supplies the needed draft. Ash drops through the grate, but many particles are carried along with the hot gases. The particles and any combustible gases are combusted in an "afterburner". The combustion product gases are further treated with acid gas scrubbers to remove hydrogen chloride, sulphuric acid and nitric acid emissions.

The rotary kiln technology is characterised by relatively long residence times (from 30 minutes up to 3 hours) of the material in the reactor obtaining a high conversion. The residence time is controlled by the rotational speed and the angle at which the kiln is positioned. The residence times of liquids and volatilised combustibles are controlled by the gas velocity in the pyrolysis system.

The temperature profile is longitudinal as well as transversal (figure 3.5). One of the advantages is that it is not important the particle size. The material introduce can be relatively big compared with a fluidized bed reactor.

Another advantages of the rotary kiln for the pyrolysis of waste:

- minimum requirements with respect to sorting and preparation of waste
- wide variety of products
- continuous pyrolysis
- no moving parts inside the kiln
- waste can be fed directly, without preparation such as preheating or mixing

The main disadvantages are:

- relatively low thermal efficiency
- the temperature gradient is big and not easy to control
- Spherical or cylindrical items may roll through the kiln before complete pyrolysis
- high maintenance costs

The pyrolysis processes that use a rotary kiln are Kobe steel and Tosco, pyrolysis of scrap tires [50], Salzgitter, Pyropleq®, pyrolysis of MSW, Contherm®, pyrolysis of MSW and automotive shredder residues (ASR), and Pyromelt, a combination of pyrolysis and slagging combustion [51].

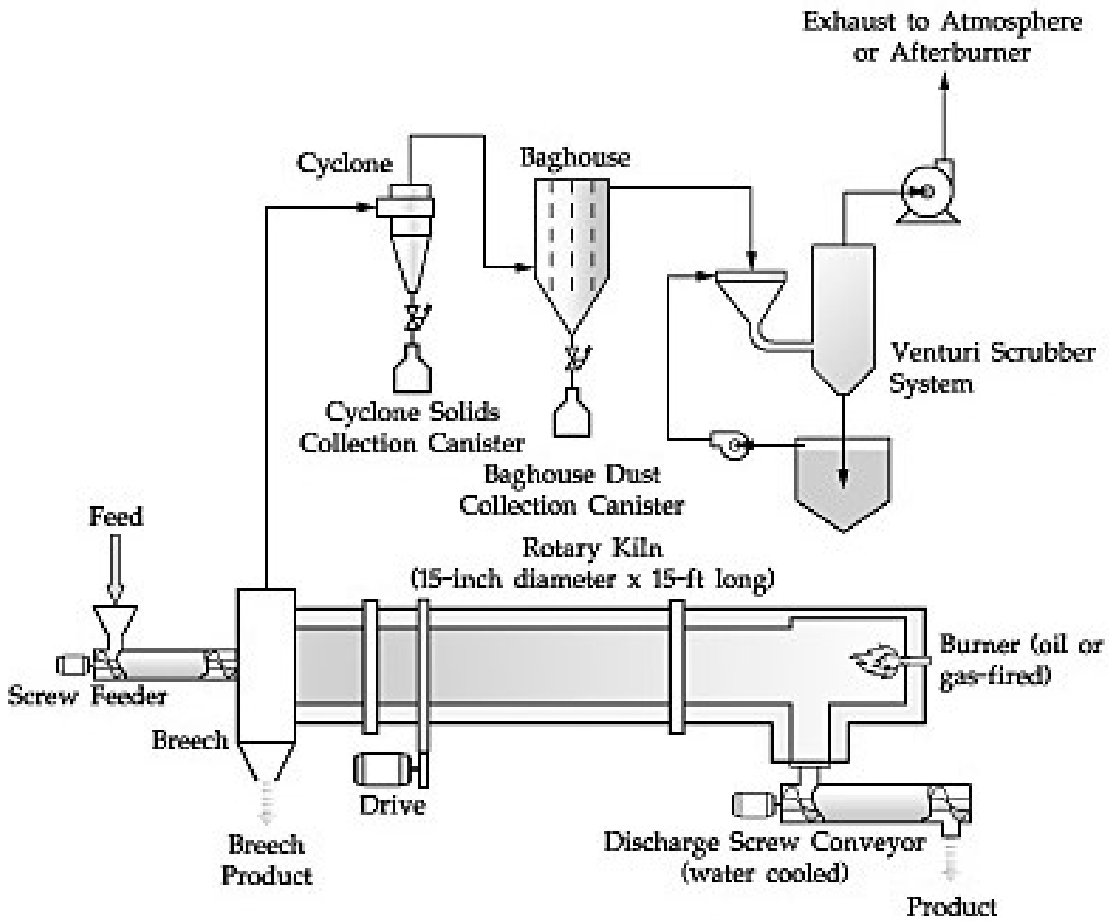


Figure 3.5.- Schema of a rotary kiln reactor for pyrolysis.

3.4.1.3. Melting vessel

One example of an industrial melting vessel reactor is the BASF feedstock recycling process. It was designed to handle mixed plastic waste that needed a pre-treatment before entering the process. The conversion of pre-treated mixed plastic into petrochemical raw materials takes place in a multi-stage melting and reduction process, carried out under atmospheric pressure in a closed system.

In the pre-treatment, the waste plastic is sorted based on physical properties such as hard, soft, films etc. and the plastic is separated from other materials. Size reduction of the sorted feed is carried out using crusher, cutter and shredder and graded into uniform size using sieves.

The sorted material is mixed and fed to the melting Vessel through a pre-heater feeder.

The first step of the conversion process is the melting of the plastic and the dehalogenation to preserve the plant's segments from corrosion. The impurities such as hard metal, sand, glass etc. settle out on the bottom of the reactor and are removed.

In the subsequent stages the melted plastic waste is heated over 400 ºC under atmospheric pressure and cracked into components of different chain lengths. About 20-30 % of gases are produced. The gaseous products from the molten plastic can be separated into HCl gas and gaseous hydrocarbons. HCl gas is separated by absorption in a water column. The yield of oils is about 60-70 %. The oil is separated in a distillation column. Naphtha produced by the feedstock process is treated in a steam cracker and the monomers are recovered and used for the production of virgin plastic. High boiling oils can be processed into synthesis gas or conversion coke and then be transferred for further use. The residue consists of 5 % minerals at most.

Disadvantageous is the really poor heat exchange of this kind of reactor presenting big temperature gradients and the difficulty to control. The residence times are always superior of 20 minutes. But the conversion efficiency is over 90 %. The range of products which can be obtained is wide and depends strongly on feed type and residence time. The quality of the products is not as high as the products produced by fluidized bed reactor. And, in the economic point of view really important, the processing cost exceed the value of the obtained products. Moreover, an installation like the melting vessel requires a full scale plant about 300.000 t/y of plastic waste to be convenient.

3.4.1.4. Mobile grate

This process is a combination of a pyrolysis chamber and a smelting furnace. Von Roll [51] has brought together both processes called the Von Roll process.

The reactor of the process (figure 3.6) is a reciprocating grate furnace as a pyrolysis chamber to convert the waste into pyrolysis gas and cokes. The waste is pyrolysed at a bed temperature of about 500°C. The pyrolysis gas leaves the chamber at 900°C. The pyrolysis coke and any unused pyrolysis gas are drawn into a smelting furnace where additional oxygen injection creates high temperatures (1400°) to melt all solid materials. The use of oxygen reduces the volume of gases formed (compared to air). Heavy metals are concentrated and separated from the molten slag. The residual slag is pelletised and can be used as a cement additive or construction material. The hot gases from the smelting furnace are combusted in a circulating fluidised bed boiler at temperatures below 1400°C. Oxygen is again added to ensure complete oxidation of organic compounds. The flue gas and the circulating sand are separated in a hot cyclone. The gases are used to generate steam for electricity and heat.

The Von Roll process was developed for improved recycling of non-combustible fractions of waste by thermal treatment under total smelting conditions. Von Roll has a long history of utilizing conventional moving grate technology for MSW dating back to the 1930s. The first RCP (Recycled Clean Product) plant for the combustion of MSW began operations in 1997 in Bremerhaven, Germany. Although the moving grate furnace and smelting technologies are well known technologies, several years were required to bring the Bremerhaven facility up to full operation. During four operation periods between June 1997 and October 1998 the plant was for about 1000 hours operating under melting conditions.

Since 1997, the plant was able to increase production processing to approximately 4,900 tons of material in 1999 and 8,600 tons of material in 2000. A 50,000 TPY per year ASR-fueled plant is also planned for Switzerland.

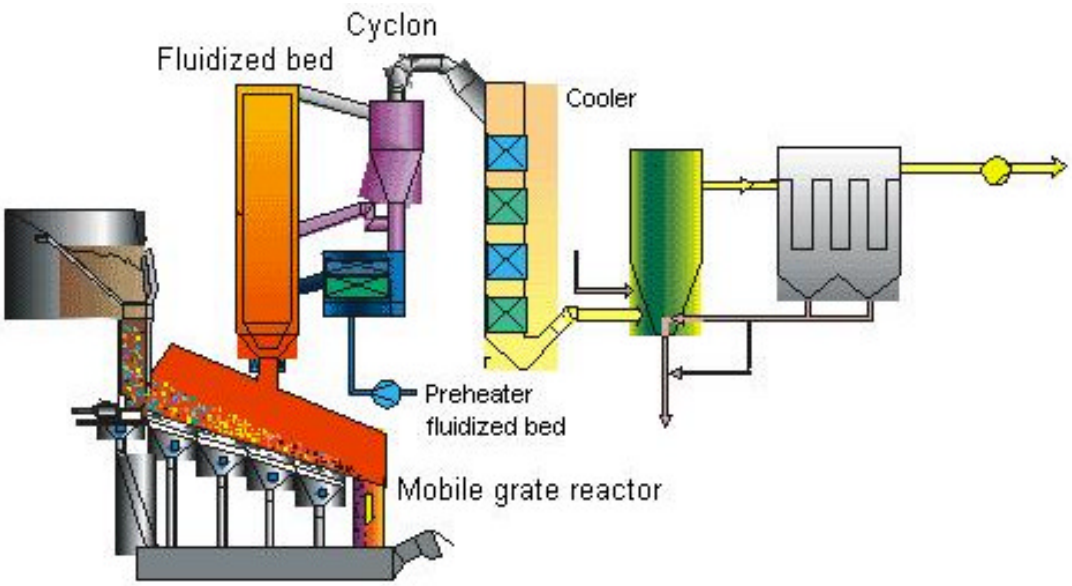


Figure 3.6.- Schema of a mobile grate reactor for pyrolysis and process.

3.4.2. Pyrolysis reaction mechanisms

The decomposition of plastics can be considered as depolymerisation of polymers into low-molecular products. The general reaction mechanism for the thermal degradation is described with the following steps:

- **Initiation** may occur at random or end-chain positions.

Random scission:

$$-CH_2-CHX-CH_2-CHX- \rightarrow -CH_2-\dot{C}HX + \dot{C}H_2-CHX-$$

End-chain scission:

$$-CH_2-CHX-CH_2-CHX \rightarrow -CH_2-\dot{C}HX + \dot{C}H_2-CHX$$

- **Depropagation** is the release of olefinic monomeric fragments from primary radicals.

$$-CH_2-CHX-CH_2-\dot{C}HX \rightarrow -CH_2-\dot{C}HX + CH_2=CHX$$

- **Hydrogen chain transfer** reaction, which may occur as intermolecular or intramolecular processes, leads to the formation of olefinic species and polymeric fragments. Moreover, secondary radicals can also be formed from hydrogen abstraction through an intermolecular transfer reaction between a primary radical and a polymeric fragment. β-cleavage of secondary radicals leads to an end-chain olefinic group and a primary radical.

Intermolecular:

$$-CH_2-\dot{C}HX + -CH_2-CHX-CH_2-CHX-CH_2- \rightarrow$$

$$\rightarrow -CH_2-CH_2X + -CH_2-CHX-CH=CHX + \dot{C}H_2-$$

$$-CH_2-\dot{C}HX + -CH_2-CHX-CH_2- \rightarrow -CH_2-CH_2X + -CH_2-\dot{C}X-CH_2-$$

Intramolecular:

$$-CH_2-CHX-CH_2-CHX-\dot{C}H_2 \rightarrow -CH_2-\dot{C}HX=CH-CHX-CH_3$$

β–cleavage:

$$-CHX-CH_2-\dot{C}X-CH_2- \rightarrow -\dot{C}HX + CH_2=CX-CH_2-$$

Formation of branches:

$$-CH_2-\dot{C}HX + -CH_2-\dot{C}X-CH_2- \rightarrow CH_2-\overset{\overset{CHX-CH_2-}{|}}{C}X-CH_2-$$

$$-CH_2-\dot{C}X-CH_2- + -CH_2-CX-CH_2- \rightarrow -CH_2-\overset{\overset{-CH_2-CX-CH_2-}{|}}{C}X-CH_2-$$

- **Termination** takes place either in a bimolecular mode with the coupling of two primary radicals or by disproportion of the primary macroradicals.

Bimolecular coupling:

$$-CHX-\dot{C}H_2 + \dot{C}HX-CH_2- \rightarrow -CHX-CH_2-CHX-CH_2-$$

Disproportionation

$$-CH_2-CHX-\dot{C}H_2 + \dot{C}HX-CH_2-CH_2- \rightarrow -CH_2-CHX-CH_3 + CHX=CH-CH_2-$$

There are 4 different decomposition reaction mechanisms of plastics proposed depending on the plastic type [52].

- End chain Scission: the polymer is cracked at the chain ends first. Then the cracking successively works down the polymeric length and individual monomer units are successively removed at the chain end. As well terminal free radicals (PMMA, PTFE, PMAN, PES, PS, PIB) are produced.
- Random chain scission: the polymer is broken up randomly into smaller molecules of varying chain lengths producing a volatile with or without double bonds (PS, PIB, PE, PP, PB).
- Chain-stripping: the reactive substituents or side up groups on the polymer chain are eliminated, leaving an unsaturated chain. This polyene then undergoes further reaction, including β-scissions, aromatisation and coke formation (PVC, PVF, PAN).
- Cross-linking: the formation of chain networks occurs from thermosetting polymers, when heated at high temperature. This is a pyrolytic condensation and a rearrangement of carbon networks to form high strength materials (Thermosetting plastics).

These different mechanisms are related to the bond dissociation energies, the chain defects of the polymer, the aromatic degree and the presence of halogen

and other hetero atoms in the polymer chains. PVC decomposes by the chain stripping mechanism with much less monomer recovery, whereas the pyrolysis of PS with cyclic structure occurs by both end-chain and random-chain scission mechanism and the monomer recovery is very high. Especially, PE and PP which comprise the main polymers in waste plastics pyrolyse by random-chain scission, which yields a wide range of hydrocarbons with low valuable products as well as lower boiling-point hydrocarbons. Thus in the pyrolysis process the cracking of high boiling point hydrocarbons to obtain valuable light oil product with high yield must be taken into consideration in a large scale plant.

3.4.2.1. Thermal

It has to be marked, that the thermal decomposition of a polymer generally involves more than one of these classes of reaction mechanisms.

Thermal cracking often yields a low-value mixture of hydrocarbons with a very broad volatility range that can extend from hydrogen to coke [53, 54]. It is therefore important to determine the optimal pyrolysis conditions and/or the most advantageous catalyst to obtain marketable products (e.g. diesel fuel) from mixed plastic wastes.

The pyrolysis product yield and composition are controlled not only by the temperature, but also by the duration of the residence time.

As a general rule of thumb; the higher the pyrolysis temperature, the higher the yield of non condensable gaseous products and the lower the yield of liquid fuels such as diesel. The optimum temperature range for the production of diesel products from waste plastics is 390-425 ºC.

Studies in a tubular reactor have highlighted the importance of short residence time with high temperature pyrolysis for obtaining a high yield of light olefins.

There is a dramatic increase in gas yield with increasing temperature of pyrolysis. While the hydrocarbon pyrolysis product yield increases with pyrolysis temperature, the yield of the oil fraction is higher at the lower pyrolysis temperatures. The composition of the pyrolysis oil also changes with pyrolysis temperature, generally containing larger quantities of aliphatic compounds at the lower temperatures than at higher temperatures where aromatics are the dominant compounds.

The polymer breakdown process is shown in figure 3.7.

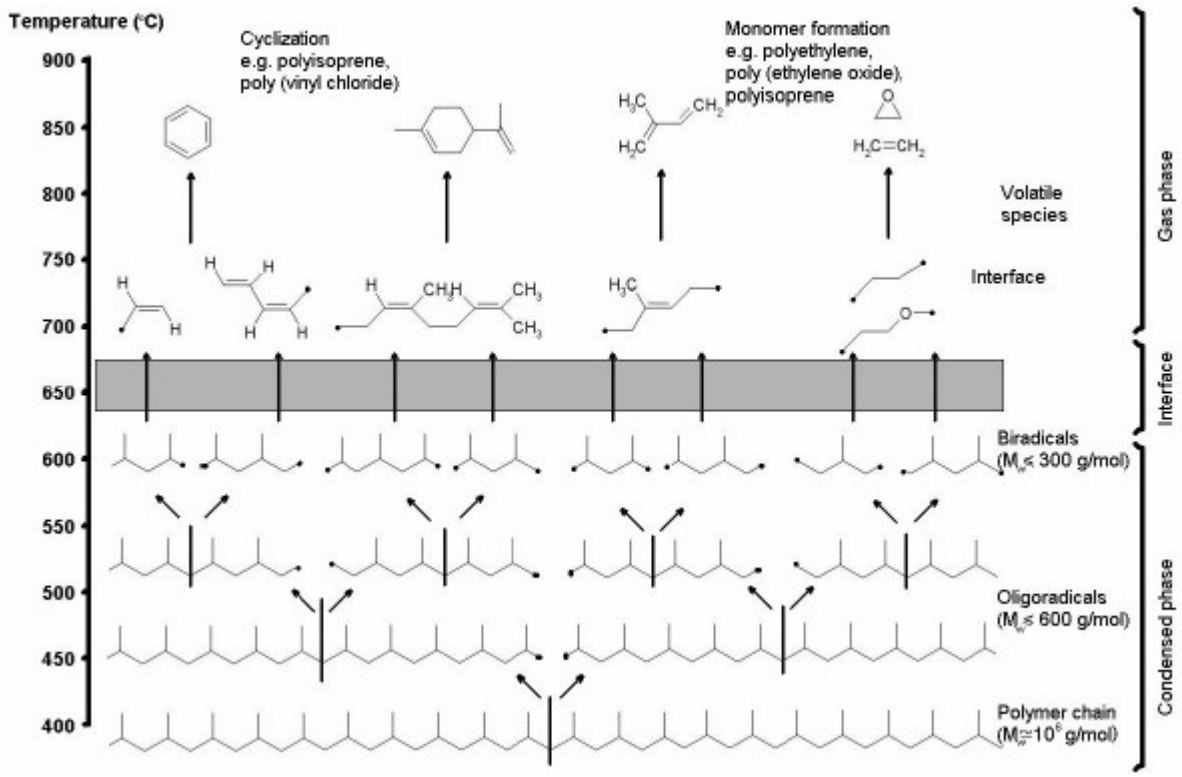


Figure 3.7.- Chemical reactions during the decomposition of organic polymers [55]

3.4.2.2. Catalytic

The poor selectivity of the thermal decomposition of polyolefins has promoted the development of catalytic cracking. Catalytic cracking lowers the pyrolysis

process temperature and lowers the boiling temperature range of the resultant liquid products. The use of molecular sieves and amorphous silica-alumina catalysts for the cracking of waste polymers into a range of hydrocarbons has been widely studied [56-60].

Catalytic cracking has some distinct advantages overt thermal cracking, such as, lowering the cracking temperature, increasing the reaction rate and increasing the production of iso-alkanes and aromatics which are desirable for diesel fuel. Suitable cracking catalyst have the ability to both substantially reduce the pyrolysis temperature and control the pyrolysis products.

Using catalysts does not only lower the activation energy, reduce the energy consumption and improve the process efficiency, but can also improve the selectivity and quality of the products produced.

Catalyst with acidic surface sites and hydrogen ion donating ability enhance the isomerization of products and thereby increase the yield of isomeric hydrocarbons that have a beneficial effect on the cetane rating and fuel quality. Catalysts having stronger acid sites of higher density are thus more effective in cracking polyolefins. However, strong acidity and large pore size both lead to faster deactivation of the catalyst. Pyrolyzing with catalysts having mild acidity and long life are preferred for the cracking of polyolefins. A major problem with using catalysts in the pyrolysis of mixed plastics is that of coke formation deactivation the catalyst over time. The cost of these catalysts also influences their selection and commercial viability.

The amount of catalyst to be added to the waste plastic for catalytic cracking is at least 5 % by weight (typically 5-10 % by weight).

The problems associated with the use of a catalyst in the pyrolysis vessel are:

- the catalyst is a consumable and therefore adds to the running cost;
- the catalyst can have a short life-cycle due to poisoning/deactivation;

- the catalyst leads to increased levels of solid residue that requires disposal.

4. AIM OF THIS WORK

Plastic's production, especially polyolefins (figure 3.1) and consumption (figure 3.2) increase day by day. All these plastics finish their useful life equally and finally they have to be removed from environment.

The disposal of this plastic waste is an important target which could be approached by the feedstock recycling coming along with the recovery of raw materials. The pyrolysis is a technical process known for years. It runs in an atmosphere without oxygen and at high temperatures. As a complementary recycling technology to the combustion, this technique is really attractive. But because of required high temperatures, under economical aspects, this process is still not viable for the industry for most plastics and feedstock.

The use of catalytical systems [43, 61-64] and the complementation of the catalytic and the thermal degradation is a way to make this recycling technology more attractive for the industry.

The current state of the investigation is the use of fluid catalytic cracking (FCC) catalysts [57, 58, 65-70]. But even it would be more economical if Ziegler-Natta catalyst components could also be used for depolymerisation of polyolefins. Ziegler-Natta catalyst are used to polymerise olefins to polyolefins at low temperatures and there is a possibility, if they can also be used for the reverse reaction to depolymerise polyolefins under mild conditions. First experiments to use Ziegler-Natta catalysts for depolymerisation of polyolefins were carried out by Basset, Uemichi and Pifer [71, 72] but with low depolymerisation rates. The present work is focused on Ziegler-Natta catalyst compounds such as titanium chlorides to reduce operation temperatures using the Hamburg Pyrolysis Process.

The following shows the results of the investigation into the disposal of polypropylene.

Studies of the pyrolysis of polypropylene [2, 73] have shown that at temperatures of 800 ºC mainly the monomer and another light hydrocarbon fractions can be recovered. When the pyrolysis temperature is decreased, heavy oil fractions increase (C9 fractions). But if the temperature is decreased to a certain minimum value, the pyrolysis reaction can not go on anymore.

In our experiments, $TiCl_3$, $TiCl_4$ and $AlCl_3$ as Ziegler-Natta catalyst compounds were used to study the products obtained regarding the temperature and the influence of the catalysts in the pyrolysis reaction .

5. RESULTS AND DISCUSSION

5.1. Installations and chemicals

5.1.1. PR-I, Pyrolysis reactor I

For the small scale and batch reactor experiments, a pyrolysis batch reactor called PR-I was run (figure 5.1). The reactor's volume is 100 ml and it is made of glass. The heating system works with an electrical resistance of 200 W. The optimal capacity of this reactor was about 10 g of material per run. Higher amounts of material in the reactor would render it useless due to the heat transfer mechanism.

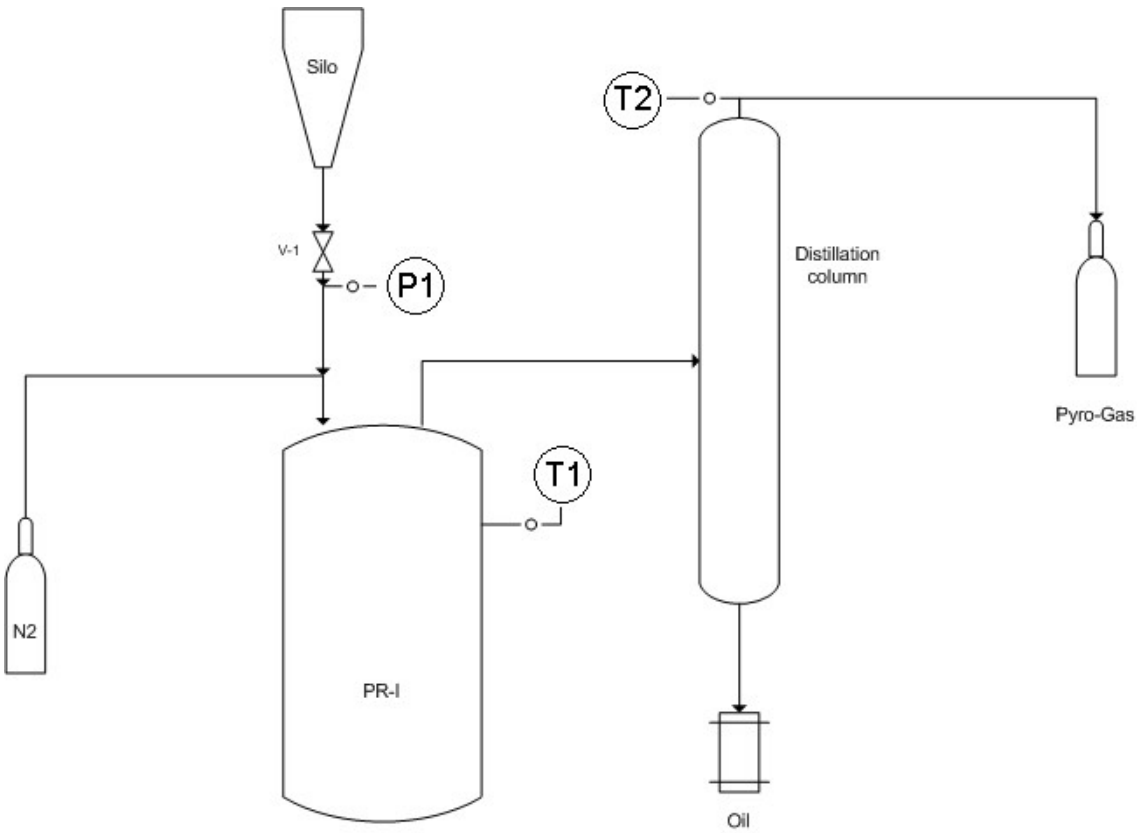


Figure 5.1.- Flow sheet of the batch reactor pyrolysis plant

The whole system worked under nitrogen atmosphere and with an overpressure of 5 mbar to ensure the transport of the product gases. The reactor was heated until the reaction temperature was reached while the material stayed in the silo. The silo was opened once the temperature was achieved, and the material fell down to the reactor. All the obtained products passed a distillation column cooled with water and a liquid nitrogen cooling trap. The oils were condensed in this trap meanwhile the gases were directed into a storage tank. The system was controlled and monitored with temperature sensors in the reactor and in the distillation column as well as a pressure sensor connected to a security valve.

5.1.2. LWS-V, Laborwirbelschichtanlage V

For the fluidised bed experiments the LWS-V reactor was used. This continuous working plant is designed in a laboratory scale for feed between 1 and 3 kg/h. Figure 5.2, shows the P&ID schema of the installation. The reactor was built with stainless steel, and the geometry of this fluidized-bed reactor is characterized by a free diameter of 154,1 mm and a height of 770 mm. The bottom part of the reactor is a porous bed where the fluid agent can go through. The plant works under overpressure (100 hPa) to ensure the inert atmosphere and to fluidize the sand [44, 74, 75]. To ensure rapid heat transfer silica sand was selected for the fluidized-bed material, having a mass of 9 kg and a particle diameter of 0,1-05 mm. The heating mechanism used for the reactor was an electrical resistance of 5 kW.

First the polymer was passed through a combination of a proportion and a water-cooled fast rotating drag-in screw to achieve a quick, constant feed into the heated fluidized bed. To reach the desired reaction temperature, the fluidizing gas was heated up in a preheater, and then directed to the reactor where the conversion of input material was finished within seconds. In order to separate the pyrolysis products, first solids like entrained sand or carbon black

were removed by cyclones. A steel condenser and two multiple coil condensers operating with ethanol to reach the temperature pf –20 ºC were used to condense the liquid products. Finally the aerosols were removed by an electrostatic precipitator. Up to the experimental operation, the cleaned gaseous products were either burned in a flare or compressed and then sent back to the reactor as fluidizing gas.

All the system presents rotameters to control the volume flow of the fluidised gases. To measure the gases produced, the system is equipped as well with gas meters and an storage system to keep the gases for analysis. The whole system is monitored with twelve temperature thermo elements and seven pressure sensors connected to a data acquisition card (Ahlborn Almemo 5990-1) and this one to computer system.

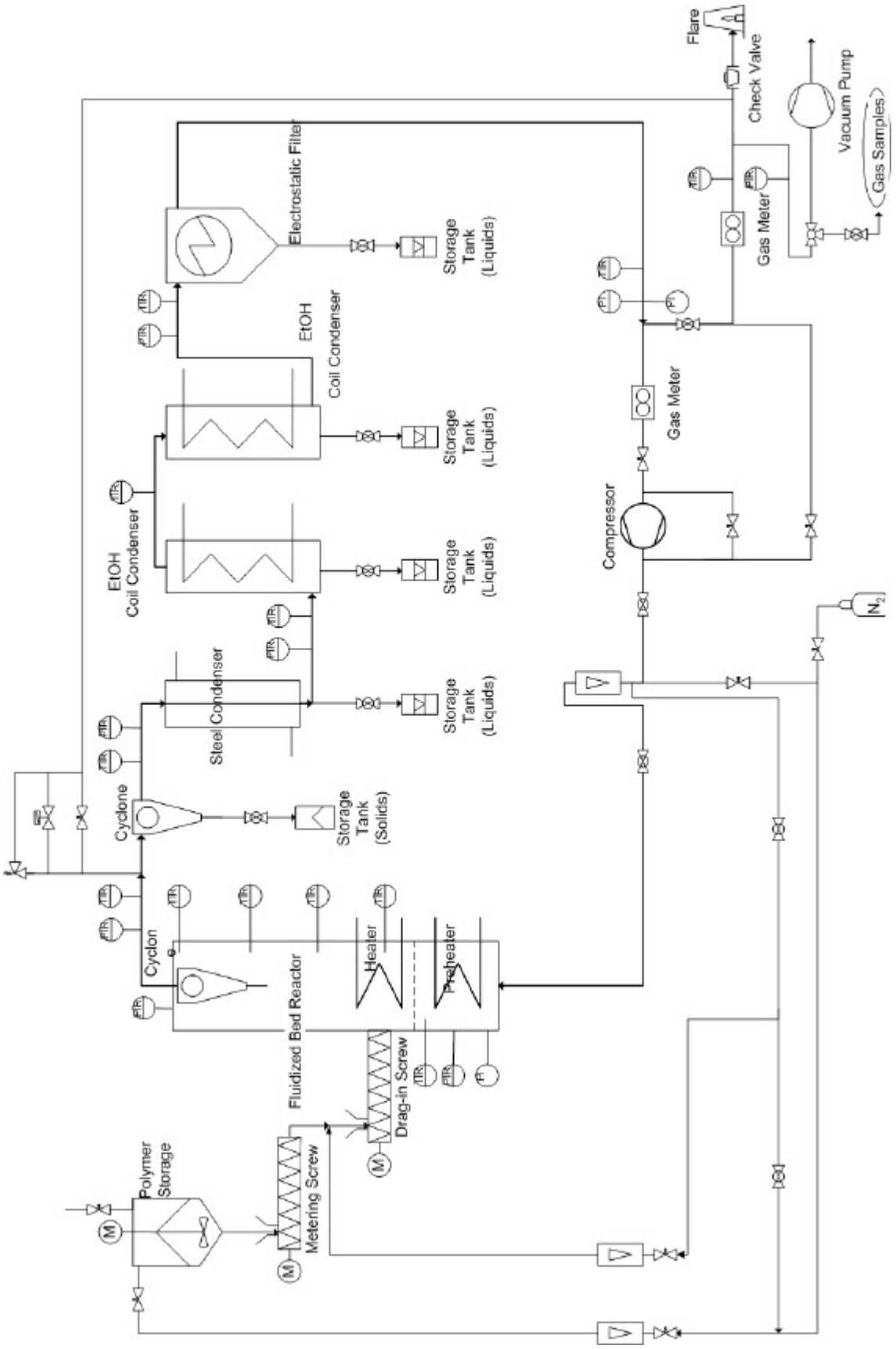
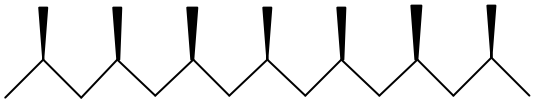


Figure 5.2.- LWS-V Flow chart

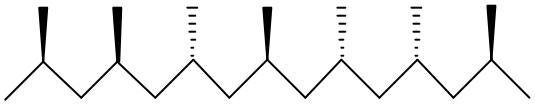
5.1.3. Polypropylene

Polypropylene is a crystalline thermoplastic and one of the major members of the polyolefins family. It is a synthetic, high molecular mass linear addition polymer of propylene. Polypropylene can be classified depending on the orientation of each methyl group CH_3 relative to the methyl groups on neighbouring monomers. This orientation has a strong effect on the finished polymer's ability to form crystals, because each methyl group takes up space and constrains backbone bending.

- Isotactic PP: Polymer formed by branched monomers that have the characteristic of having all the branch groups on the same side of the polymeric chain. The monomers are all oriented in the same way.



- Atactic PP: The CH_3 substituent belonging to a repeating unit is placed randomly at either side of the backbone.



- Syndiotactic PP: is a tacticity essentially comprising alternating enantiomeric configurational base units which have chiral or prochiral atoms in the main chain in a unique arrangement with respect to their adjacent constitutional units. In a syndiotactic PP, the configurational repeating unit consists of two configurational base units that are enantiomeric.

Polypropylene's strength and versatility stem from a matrix of interlocking crystallites that allow formation of rigid and tough articles. Highly isotactic polymer, with its regular structure, forms a helical coil having three monomer

units per turn. These coils stack together into thin lamellar crystallites which force the chains to fold several times as they emerge and reenter lamellae. While the equilibrium (i.e., thermodynamic) melting point is 188 °C, at normal analysis heating rates the final melting point is ca. 160 – 170 °C.

The polypropylene used for the conducted experiments was a polypropylene from Shell chemical which is called *"Shell Chemical 42609".* The physical properties are described below:

- Melting point: 150 ºC measured with a Differential-Scanning-Calorimetry. The curve obtained is shown in figure 5.3.

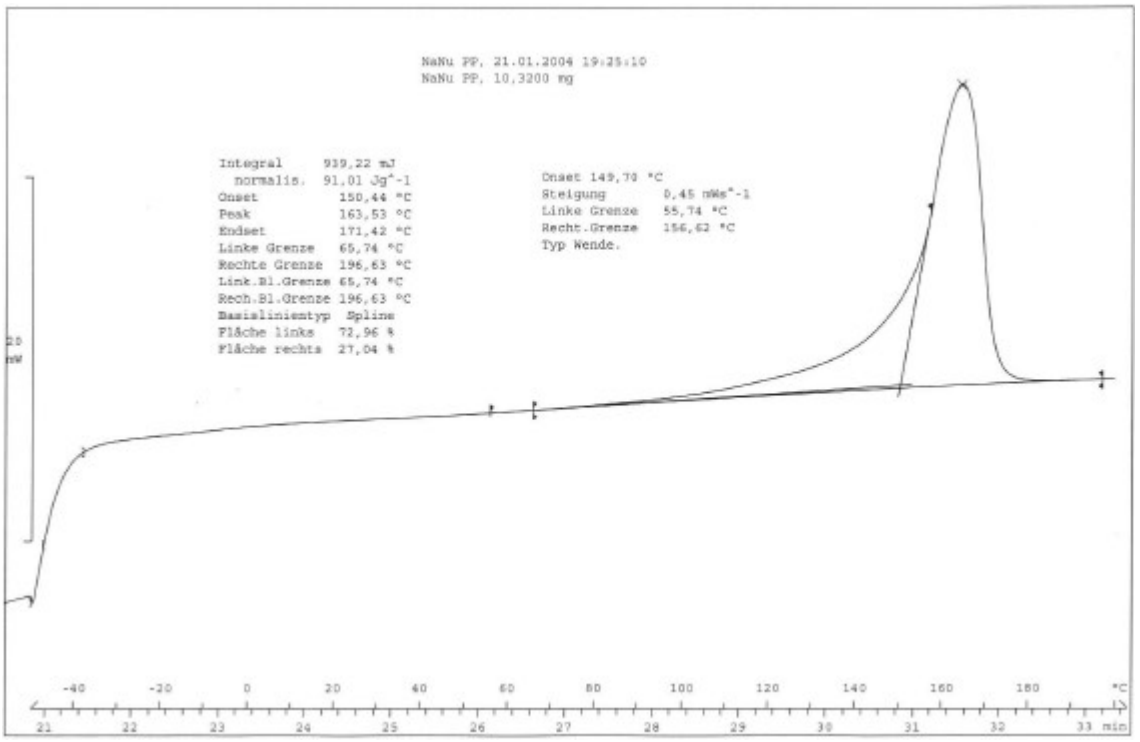
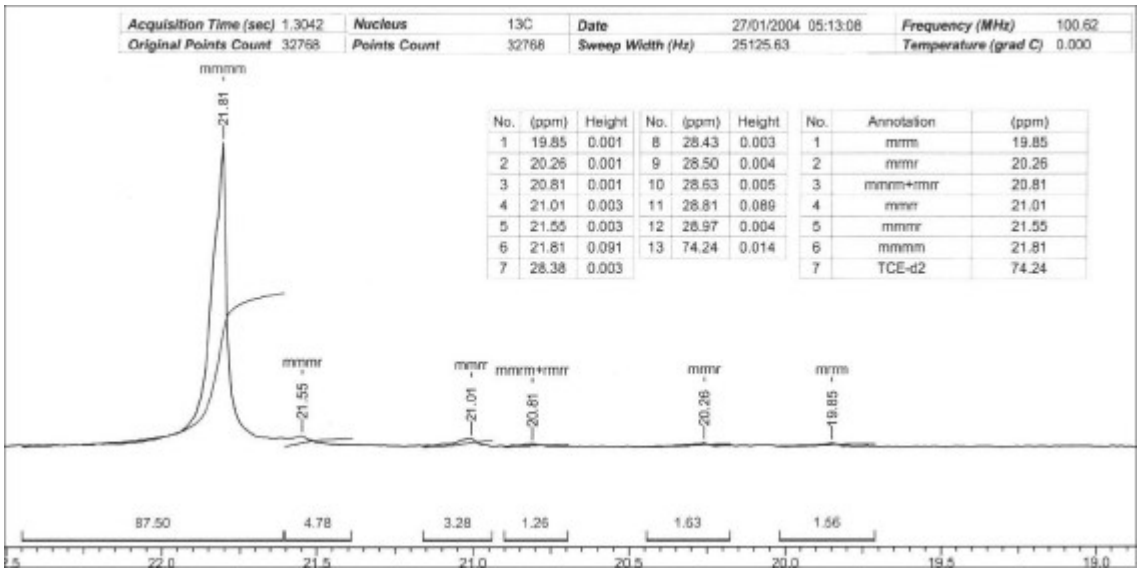


Figure 5.3.- DSC diagram of the polypropylene analysis

- The molecular weight of the polymer was 316.431 g/mol and was determined by Gel-Permeation-Chromatography.

- ≅ 90 % of the polymer chain has a isotactic distribution of the methyl groups. The analysis was carried out with ^{13}C-NMR (figure 5.4).



No.	(ppm)	Height	No.	(ppm)	Height
1	19.85	0.001	8	28.43	0.003
2	20.26	0.001	9	28.50	0.004
3	20.81	0.001	10	28.63	0.005
4	21.01	0.003	11	28.81	0.089
5	21.55	0.003	12	28.97	0.004
6	21.81	0.091	13	74.24	0.014
7	28.38	0.003			

No.	Annotation	(ppm)
1	mrm	19.85
2	mmr	20.26
3	mmm+mmr	20.81
4	mmrr	21.01
5	mmmr	21.55
6	mmmm	21.81
7	TCE-d2	74.24

Figure 5.4.- ^{13}C-NMR curve of the polypropylene *Shell Chemical 42609*

5.1.4. Fluidization sand

For the LWS-V experiments, the fluidized agent was silica sand due to the relatively inert properties and its physical resistance. As well silica is a good heat transfer medium [76]. The diameter was between 0,1 to 0,3 mm and between 0,3 to 0,5 mm depending on the experimental conditions. To obtain such a constant diameter the silica had to be sieved. Then the sand could be introduced in the reactor.

5.1.5. $TiCl_3$, Titanium (III) chloride

$TiCl_3$ is an ionic compound, comprised of one titanium and three chlorine atoms. It is a red-violet salt and Ti(III) has one unpaired electron. The violet colour arises because of the transition of this sole electron within the 3d orbital [77].

Formula as commonly written: $TiCl_3$

CAS registry number: [7705-07-9]
Formula weight: 154.225

Physical properties:

- Colour: red-violet
- Appearance: crystalline solid
- Melting point: 425°C (decomposes)
- Density: 2700 kg m^{-3}

An elementary analysis shows:

- Cl 68.96 wg %
- Ti 31.04 wg %

5.1.6. $TiCl_4$, Titanium (IV) chloride

$TiCl_4$ is a dense, colourless (or pale yellow) distillable liquid, although crude samples can be reddish-brown [77]. It is one of the rare transition metal chlorides that is liquid at room temperature. This distinctive property arises from the fact that $TiCl_4$ is molecular, that is the reason why each $TiCl_4$ behaves independently. But most metal chlorides are polymers, the chloride atoms of which bridge between the metals. The attraction between the individual $TiCl_4$ molecules is weak, primarily van der Waals forces, and these weak interactions result in low melting and boiling points. $TiCl_4$ is tetrahedral. Typical of a non-polar species, $TiCl_4$ is soluble in toluene and chlorocarbons.

The main problem with handling $TiCl_4$, beside its tendency to release corrosive hydrogen chloride, is the formation of titanium oxides and oxychlorides. $TiCl_4$ is a very aggressive Lewis acid, exothermically forming adducts with even weak bases such as THF and explosively with water, again releasing HCl.

Formula as commonly written: $TiCl_4$
CAS registry number: [7550-45-0]
Formula weight: 189.678

Physical properties

- Colour: colourless to yellow
- Appearance: liquid
- Melting point: -24°C
- Boiling point: 136.5°C
- Density: 1730 kg m^{-3} (liquid)

An elementary analysis shows:

- Cl 74.76 wg %
- Ti 25.24 wg%

5.1.7. $AlCl_3$, Aluminium (III) chloride

$AlCl_3$ is a solid with a low melting and boiling point. It is also covalent. $AlCl_3$ sublimes at 178 °C and presents a six-coordinate layer lattice.

Melting $AlCl_3$ gives the dimer Al_2Cl_6, which can vaporise. At higher temperatures this Al_2Cl_6 dimer dissociates into trigonal planar $AlCl_3$.

Aluminum chloride is highly deliquescent, and it can explode in contact with water because of the high heat of hydration. It partially hydrolyses with H_2O, forming some hydrogen chlorides and/or hydrochloric acid. Aqueous solutions of $AlCl_3$ are fully ionised, and thus conduct electricity well. Such solutions are found to be acidic, indicating that partial hydrolysis of the Al^{3+} ion is occurring.

AlCl3 is a powerful Lewis acid, capable of forming stable Lewis acid-base adducts with even weak Lewis bases such as benzophenone or mesitylene. It is probably the most commonly used Lewis acid and also one of the most powerful. It finds widespread application in the chemical industry as a catalyst. It also finds use in polymerisation and isomerisation reactions of hydrocarbons.

Formula as commonly written: $AlCl_3$
CAS registry number: [7446-70-0]
Formula weight: 133.34

Physical properties

- Colour: white
- Appearance: crystalline solid
- Melting point: 192.6°C
- Boiling point: 180°C
- Density: 2480 kg m^{-3}

An elementary analysis shows:

- Al 20.24 wg %
- Cl 79.76 wg %

5.2. Polypropylene pyrolysis

Polypropylene decomposes at temperatures between 400 ºC and 470 ºC. The pyrogram of an isotactic PP displayed in figure 5.5 shows that the most important components of the degradation are trimer, tetramers and pentamers of propylene, boiling in the gasoline range. The oligomers of propylene are isoalkenes joining the propylene units at the second and third carbon atoms similarly to PP. The observed pyrolysis product distribution of PP is arised from

a free radical mechanism [78-80] which begins with the homolytic breakage of the polymer chain.

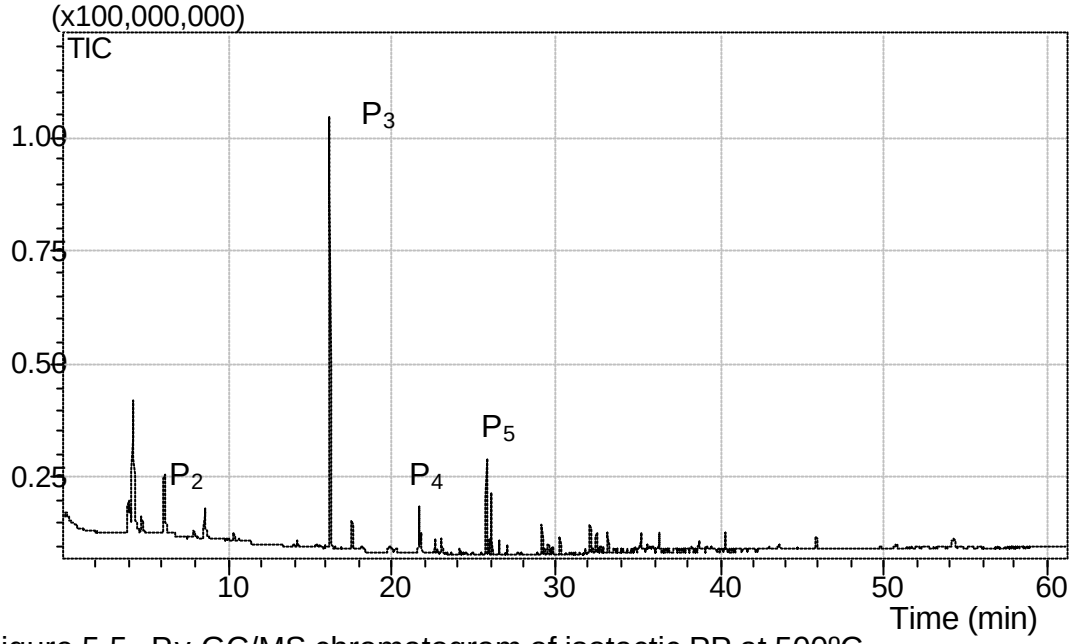


Figure 5.5.- Py-GC/MS chromatogram of isotactic PP at 500ºC

The tertiary carbon sites in PP allows the facile chain cleavage and rearrangements according to the Rice-Kossiakoff cracking mechanism shown in figure 5.6 [81].

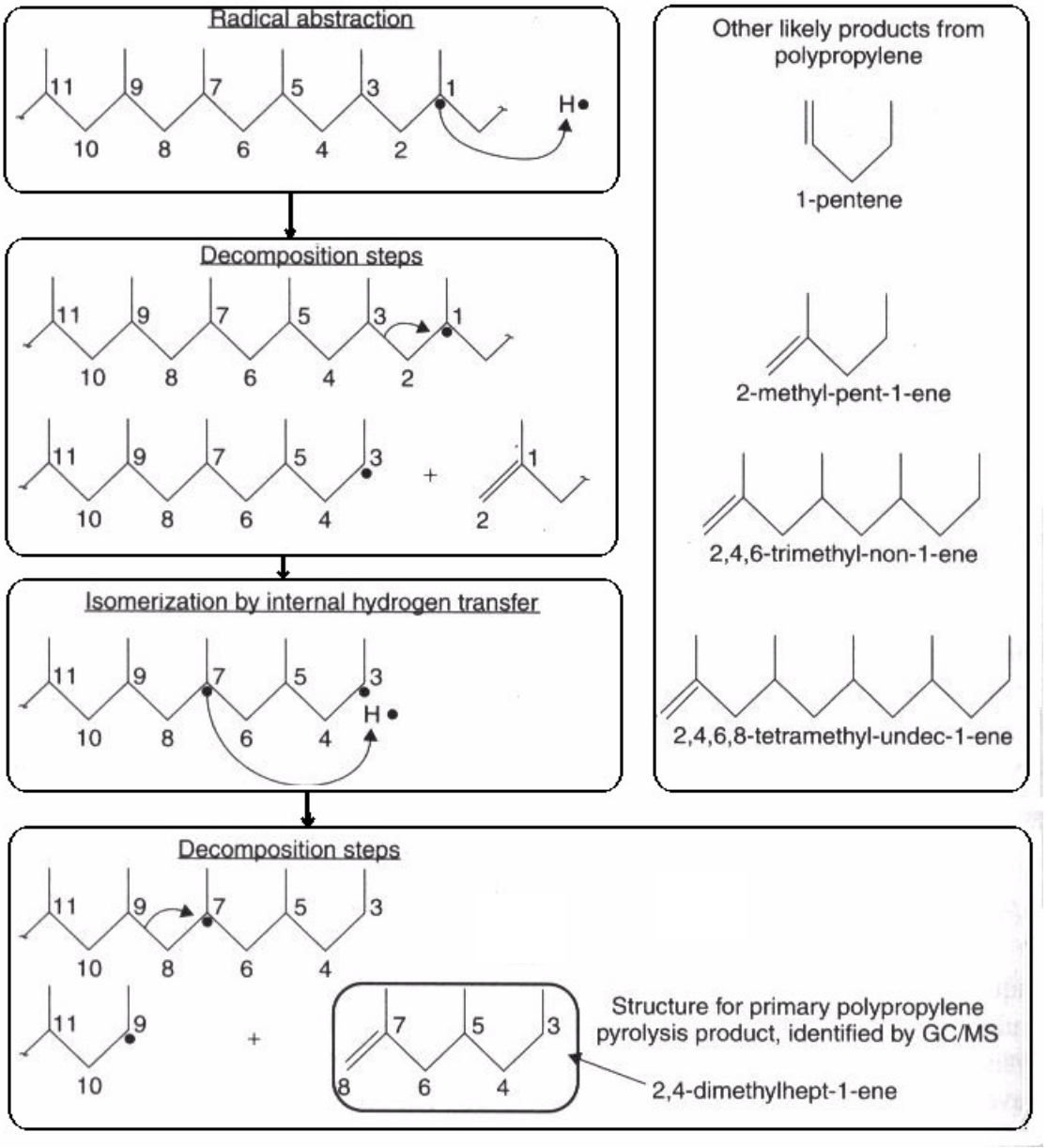


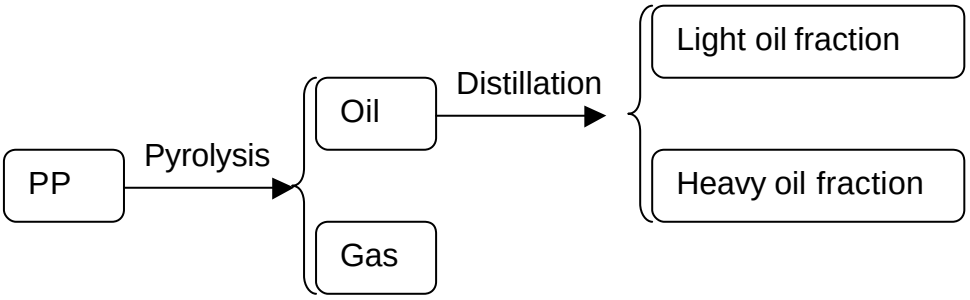
Figure 5.6.- Rice-Kossiakoff cracking mechanism for polypropylene showing that the pyrolysis products of PP retain a branched structure

The non-condensable gas from PP pyrolysis contains elevated levels of propylene, isobutylene and n-pentane.

The PP pyrolysis produces less coke residue compared with PE, and more liquid products. In the pyrolysis process of PP the intramolecular radical transfer is preferred to the intermolecular one, thus the low oligomer formation predominates, skewing the carbon number distribution towards the light end of the distillate spectrum. Consequently the pyrolysis oil of PP is much more

volatile than that of PE, which is decomposed mainly through intermolecular radical transfer. The difference in the backbone structure of the products of these polymers is more important from the point of view of fuel properties. The isoalkanoic structure of PP is maintained in the thermal decomposition products, therefore the octane number of the pyrolysis oil is typically high.

The PP pyrolysis protocol followed in the present work is:



All the pyrolysis products obtained were separated in a gas stream directed into a storage tank and in a liquid stream. The liquid fraction, was distilled. Due to high temperatures needed (300 °C) for the distillation under atmospheric pressure conditions, secondary reactions could occur. In order to avoid this, the distillation was carried out under vacuum conditions (3 mbar) up to 160 °C according to the vapour-liquid equilibrium of fluorine (C13).

The gas fraction was analysed quantitatively by gas chromatography with a flame ionisation detector (GD-FID, Chrompack CP 9002, Chrompack CP-Al_2O_3/KCl-Plot) for the hydrocarbons and by gas chromatography with a thermal conductivity detector (GC-TCD, Chrompack CP 9001, Chrompack Carboplot® P7) for the permanent gases (N_2, H_2, CO, CO_2). Both measurements were correlated via methane and the response factors of the hydrocarbons were calculated. The qualitative analysis of the hydrocarbons was carried out by gas chromatography with mass spectrometer (GC-MS, GC:HP 5890, MS: Fisons Instruments VG 70 SE, Chrompack CP-Al_2O_3/KCl-Plot).

The oil fraction was characterised by GC-FID (HP 5890, Macherey & Nagel SE 52) and GC-MS (GC:HP 5890, MS: Fisons Instruments VG 70 SE, Macherey & Nagel SE 52) and the results were covered by an elementary analysis (Carlo Erba CE 1106 CHNS-O, following DIN 51721). The water content was determined by titrating following the Karl-Fischer method (Methrom E 547, ISO 8534). A simulated distillation column was used to characterise the tar fraction (GC-FID, HP 5890 SII, Varian WCOT Ulti-Metal CP SimDist CB).

5.2.1. Pyro-GC/MS

Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) is an instrumental method that enables a characterisation of non-volatile macromolecular complexes found in virtually all materials in the natural environment. It differs from GC/MS in the type of sample analysed and the method by which it is introduced to the GC/MS system.

The history of this device starts in 1948 when Madorsky and Straus [82] as well as Wall [83] reported the investigation of bonds between high molecular weight molecules via off-line pyrolysis-mass spectroscopy. Five years later Bradt et al. [84] presented a pyrolysis unit associated to a mass spectrometer being possible to obtain direct information about the structure of the samples making the measurements under vacuum conditions. In 1952 James and Martin introduced a gas chromatographer device [85]. Consequently the components of a pyrolysis reaction could be separated in the analytical column of the GC and GC/MS proceeds as normal. Later mixtures of gas from the pyrolysis of polyolefins with more than 100 components could be measured by being directed through capillary colums with high resolution (Golay [86]). In 1979 Dandenau [87] used therefore capillary columns made of silica and additionally an inert reagent.

The modern Py-GC/MS systems include mass spectrometers, gas chromatographers and pyrolysers that give the possibility to analyse the samples on-line.

In the present work a pyro-gc/ms device was used due to the possibility to obtain first results in a short period of time giving an overview of the products obtained in the pyrolysis reaction in a small scale [88]. Figure 5.7 shows the diagram of the pyrolyser used for the preliminary experiments.

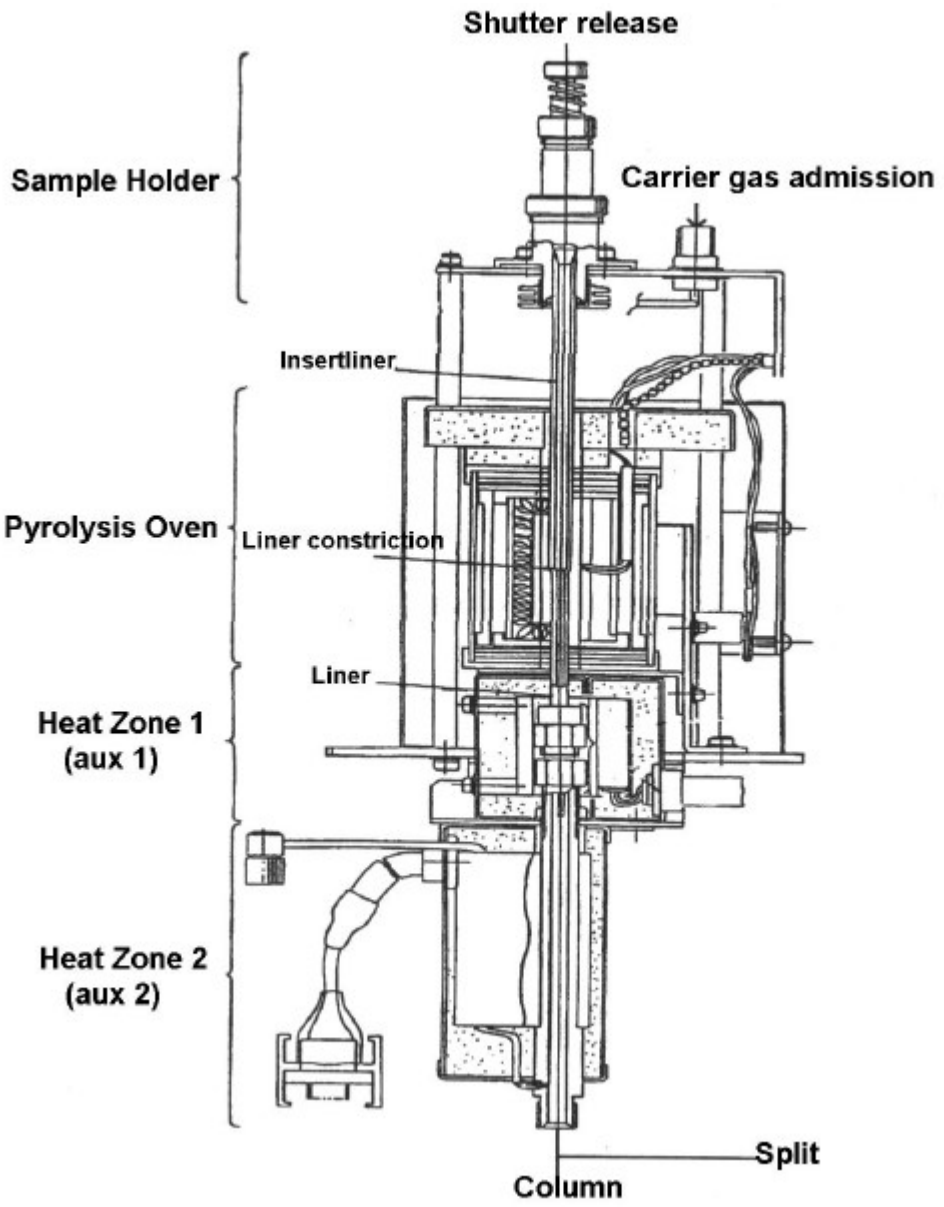


Figure 5.7.- Diagram of the pyrolyser with the infrared heater.

For the experiments carried out in that device, samples of PP with a weight from 10 µg to 100 µg were prepared in platinum buckets. These are placed in the sample holder and shot into the pyroliser starting the analysis. The pyrolysis temperature of the experiments was from 300 ºC up to 800 ºC in steps of 30 ºC. The gas chromatographer was programmed as shown in figure 5.8:

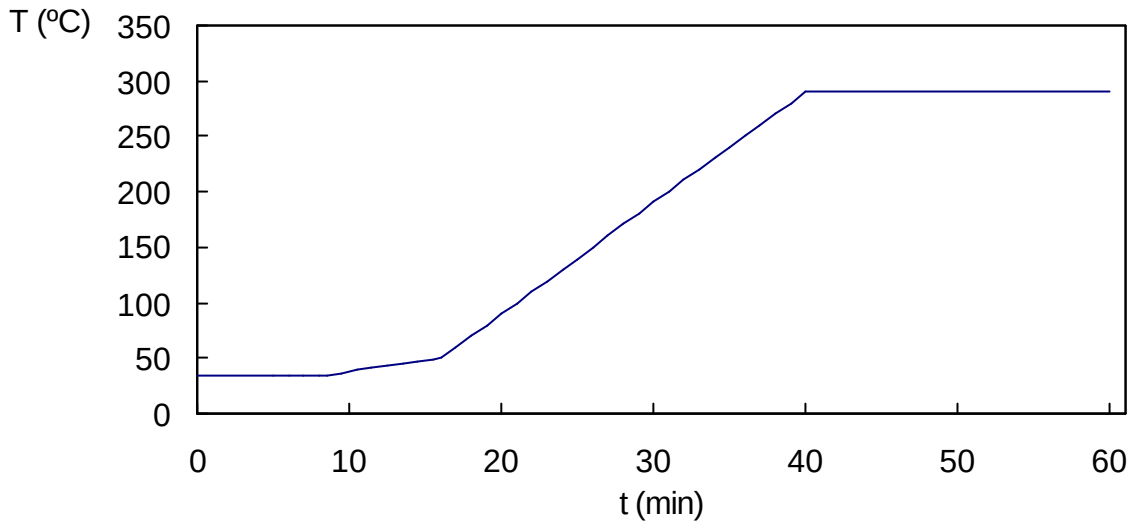


Figure 5.8.- Temperature program of the Py-GC/MS

Setting the temperature of the pyrolysis oven at 300 ºC, the pyrogram is the following one (figure 5.9):

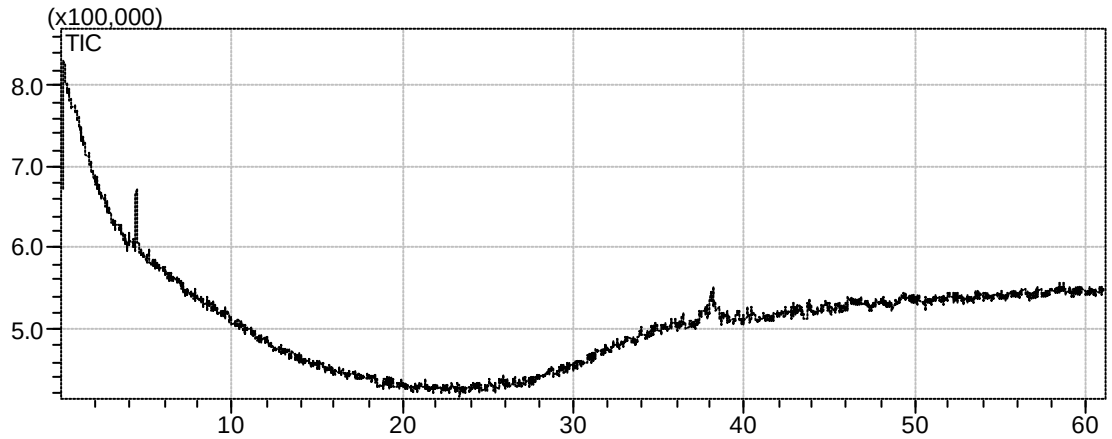
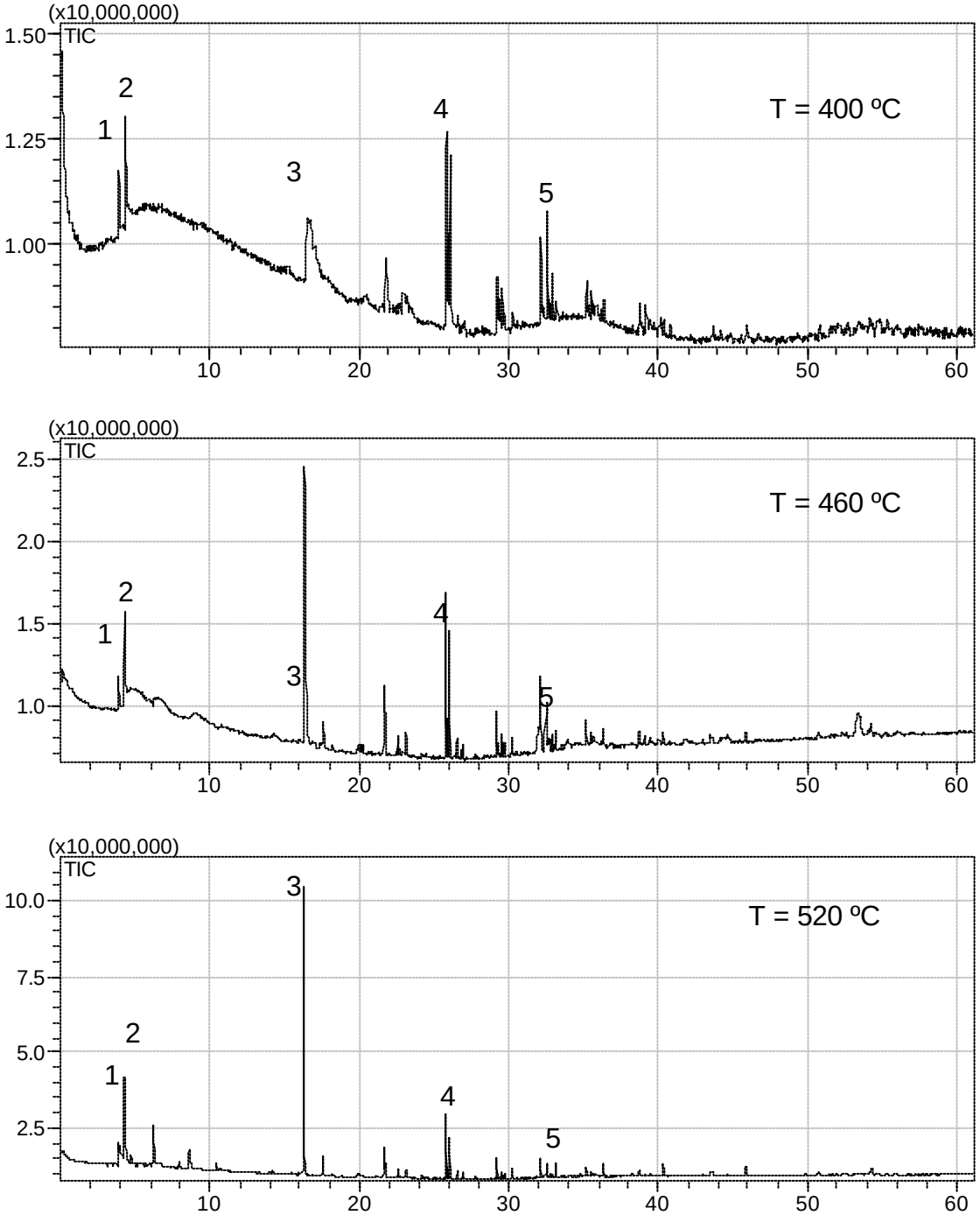


Figure 5.9.- Pyrogram of PP at 300 ºC

It can be concluded that at a pyrolysis temperature of 300 ºC PP is not decomposed.

But increasing the pyrolysis temperature, the thermal decomposition of PP is possible and can be observed by Py-GC/MS. The programs (figure 5.10) show the components produced in the pyrolysis of PP.



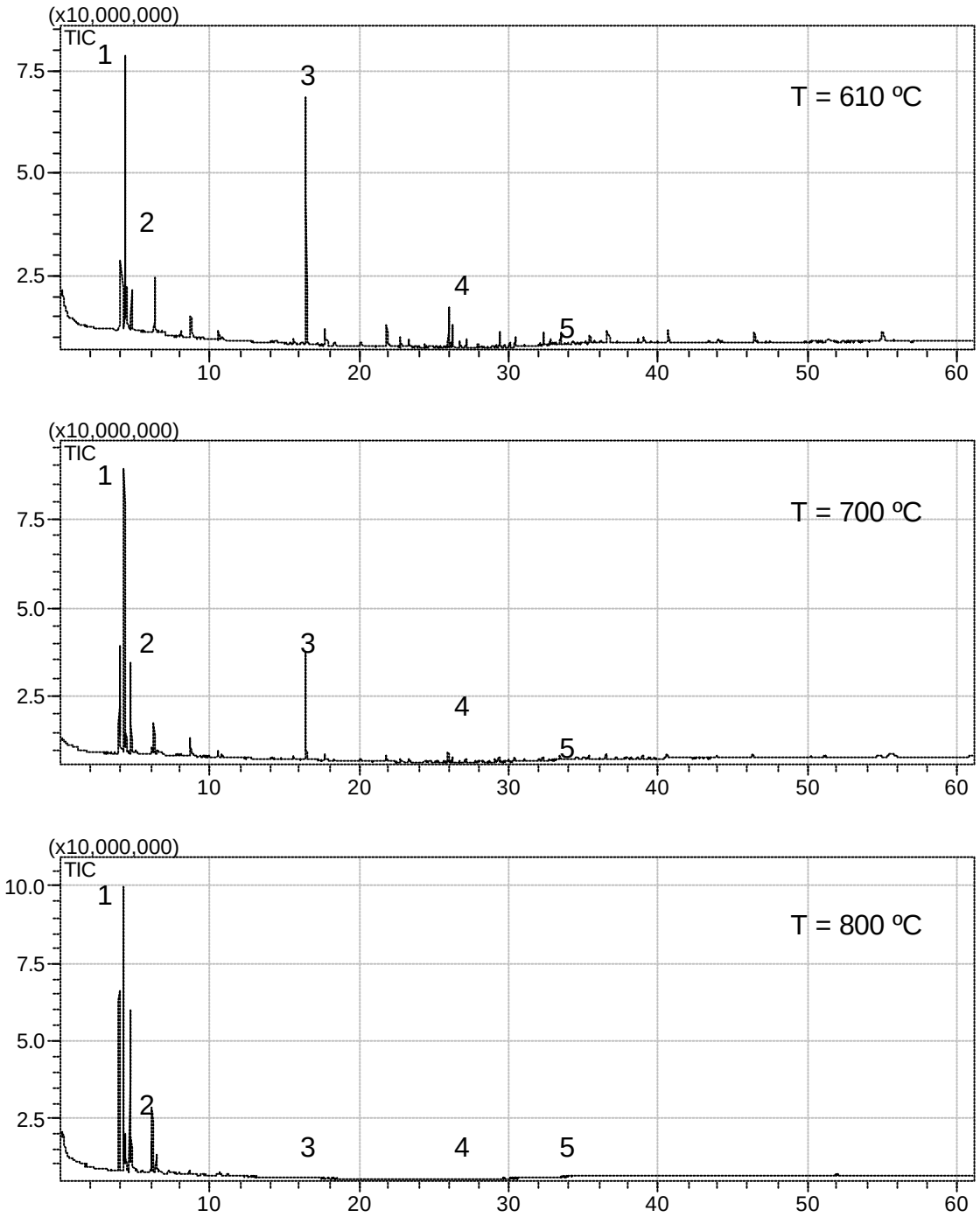


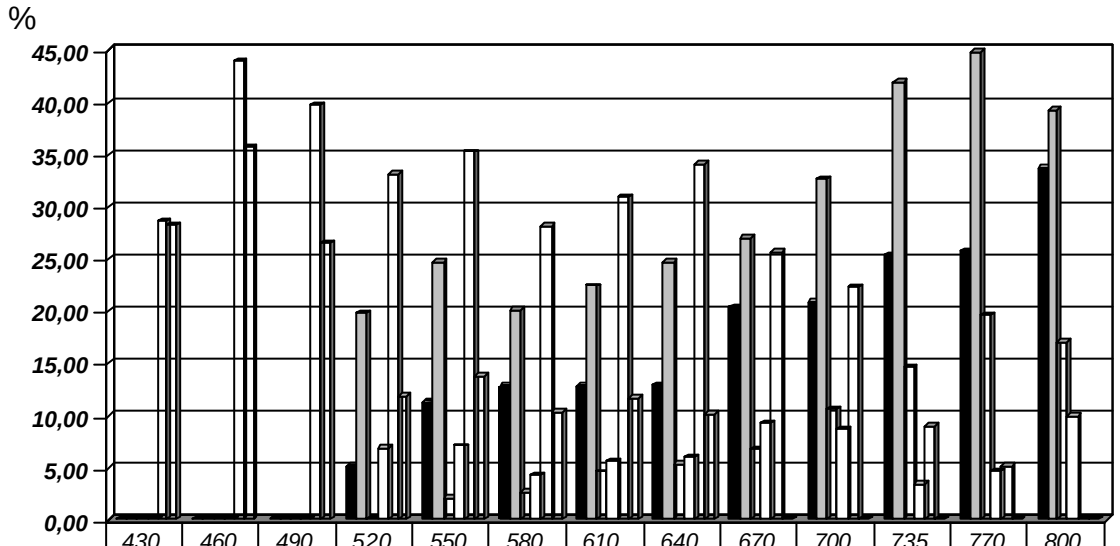
Figure 5.10.- Pyrograms of PP at different temperatures; the peaks numbers correspond with 1: Propylene; 2: 1-Pentene; 3: 2,4-Dimethyl-1-heptene; 4: 7-Methyl-1-undecene; 5: 3-eicosene

At 400 ºC starts the decomposition of PP (figure 5.11).

The amount of high molecular weight products is 28.71 % and 28,25 % (peaks on the right side) for fractions between C_6 and C_{11}, and C_{12} and C_{20}

respectively. At 520 ºC the main product generated appears really clear in the program, showing a retention time of 16 minutes and an amount of ~33 wt%. This peak corresponds with the trimer 2,4-Dimethyl-1-heptene [78, 89, 90]. With higher degradation temperatures (800 ºC) it is even possible to recover amounts of monomer (propene) of ~44 %.

The effect of the reaction temperature on the product yield is presented in figure 5.11.



	430	460	490	520	550	580	610	640	670	700	735	770	800
C2	0,00	0,00	0,00	5,15	11,33	12,80	12,83	12,89	20,40	20,87	25,41	25,72	33,66
C3	0,00	0,00	0,00	19,72	24,69	20,14	22,41	24,66	27,02	32,78	42,02	44,94	39,41
C4	0,00	0,00	0,00	0,00	2,08	2,59	4,56	5,32	6,71	10,53	14,53	19,58	16,95
C5	0,00	0,00	0,00	6,82	7,00	4,21	5,52	6,04	9,22	8,68	3,46	4,65	9,98
C6-C11	28,71	44,00	39,78	33,18	35,31	28,16	30,91	34,16	25,66	22,28	8,98	5,10	0,00
C12-20	28,25	35,82	26,60	11,76	13,83	10,27	11,67	10,16	0,00	0,00	0,00	0,00	0,00

Figure 5.11.- Effect of reaction temperature on product yield

5.2.2. PR-I

44 experiments were carried out in the batch reactor PR-I as shown in table 5.1. Only one parameter was changed in each experiment keeping other parameters

at their default to observe the influence of such variable in the pyrolysis reaction. The parameters modified were:

- Pyrolysis temperature
- Type of catalyst
- Amount of catalysts
- Ratio between catalysts in the $TiCl_4$:$AlCl_3$ mixture experiments

Table 5.1.- Experiment parameters in the PR-I experiments.

Reactor	Catalyst	Ratio (weight)	Amount (wt %)	Temperature (ºC)
PR-I	WOC			400
				500
	$TiCl_3$		0,1	350
				400
				500
			1,0	350
				400
				500
			5,0	350
				400
				500
	$TiCl_4$		0,1	350
				400
				500
			1,0	350
				400
				500
			5,0	350
				400
				500
	$AlCl_3$		0,1	300
				400
				500
			1,0	250
				300
				400
				500
			5,0	250
				300
				400
				500
	$TiCl_4$:$AlCl_3$	1:1	0,1	300
			1,0	300
			5,0	250
				300
				400
		1:5	0,1	300
			1,0	300
			5,0	250
				300
		5:1	0,1	300
			1,0	300
			5,0	250
				300

5.2.2.1. Without catalyst (WOC)

The first experiments carried out in the present work were those without catalyst. With these preliminary steps it was possible to fix, improve and to optimise the reactor; the reactor conditions were simpler (no problems with the reactivity or the mixture of catalysts). Further, it was possible to take the results obtained in the Pyro-GC/MS experiments, as well in the literature [78, 89, 90].

5.2.2.1.1. Experimental conditions

3 experiments were conducted without catalysts. Table 5.2 shows the experimental parameters. It can be observed that the minimum temperature needed to pyrolyse PP is 400 ºC. Experiments which were run at a temperature of 350 ºC showed that pyrolysis products could not be produced after even one hour of reaction.

Table 5.2.- Experimental parameters

Catalyst	wt % cat.	T (ºC)	Total input material (g)	wt % pyrolysed PP	wt % gas	wt % light oil fraction	wt % heavy oil fraction	wt % not pyrolysed PP
WOC		**350**	10,00	-	-	-	-	-
		400	10,00	57,50	10,00	12,10	35,40	42,50
		500	10,00	100,00	20,56	62,21	17,24	0,00

5.2.2.1.2. Products

Figure 5.12 indicates the 3 fractions obtained in the degradation reaction. The gas fraction obtained directly from the reaction was put into storage. The light oil fraction was obtained after the vacuum distillation, and the heavy oil fraction corresponds with the fraction not distilled.

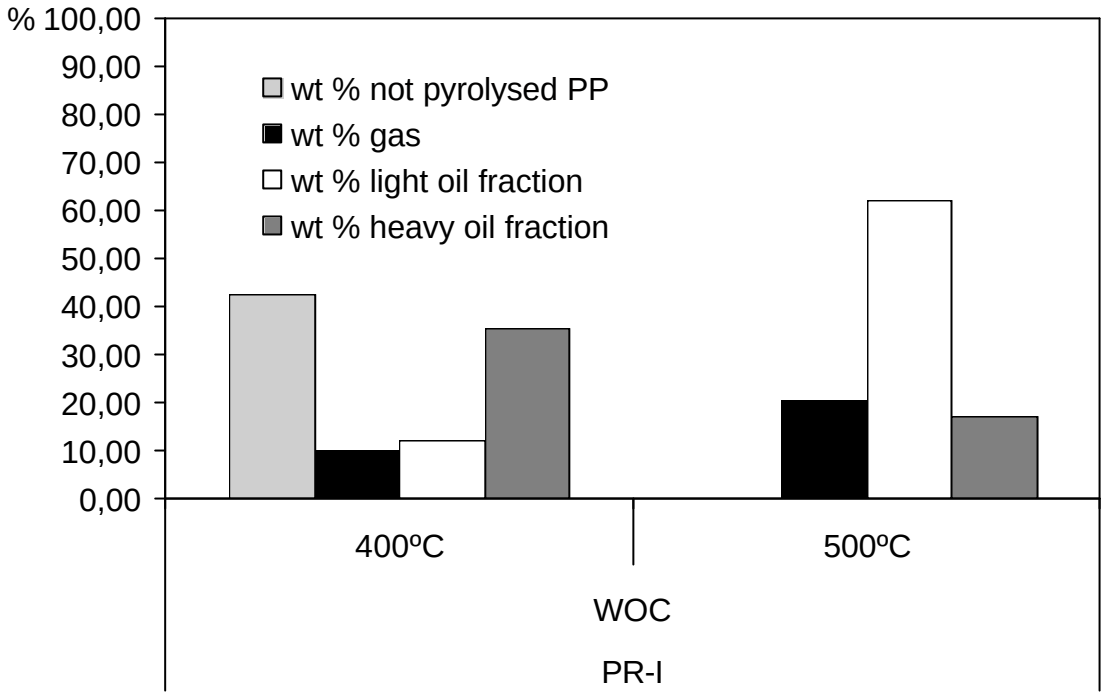


Figure 5.12.- Products distribution (wt %) of polypropylene's pyrolysis

At 400 ºC and after one hour of reaction, still there was 42,50 wt% of melted PP in the reactor. 57,50 wt% of PP was pyrolysed, more than 35 % of which corresponded with a high boiling point fraction (>C13).

Whereas after 10 minutes of reaction at 500 ºC, the amount of pyrolysed material was already close to 100 wt%. The main fraction obtained under these conditions was the light oil fraction (C5 < light oil < C12) with an amount of 62.21 wt%. But also the gas fraction was important with 20,56 wt%.

Figure 5.13 shows the different carbon number fractions in wt% obtained in the processes.

At 400 ºC was largely produced a big fraction of high boiling point hydrocarbons. These kind of products are not attractive enough to obtain in the economical point of view (less expensive than gasoline fractions). The second in importance was the C9 fraction with 4,69 wt% of the total amount. The rest of the fractions is not represented in high amounts (lower than 5%).

The results obtained after running the pyrolysis reaction at 500 ºC show that the main fraction obtained was the C9 fraction now (27.62 wt%, gasoline fraction), especially the trimer 2,4-Dimethyl-1-heptene (24,88 wt%, see figure 5.14).

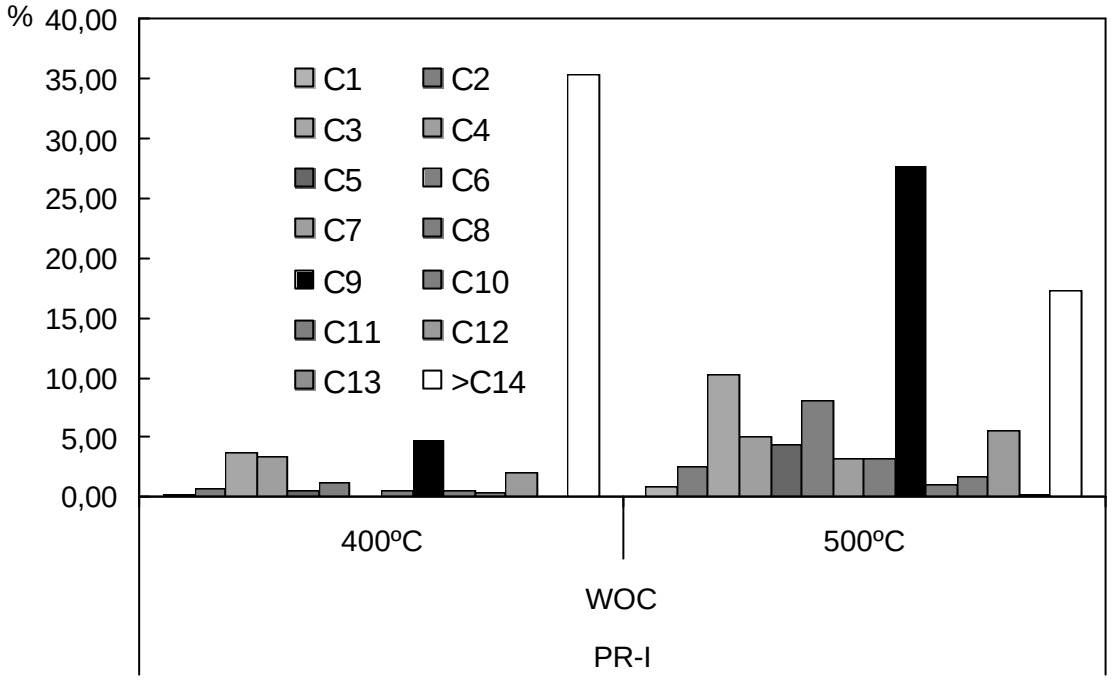


Figure 5.13.- Product fractions of polypropylene's pyrolysis

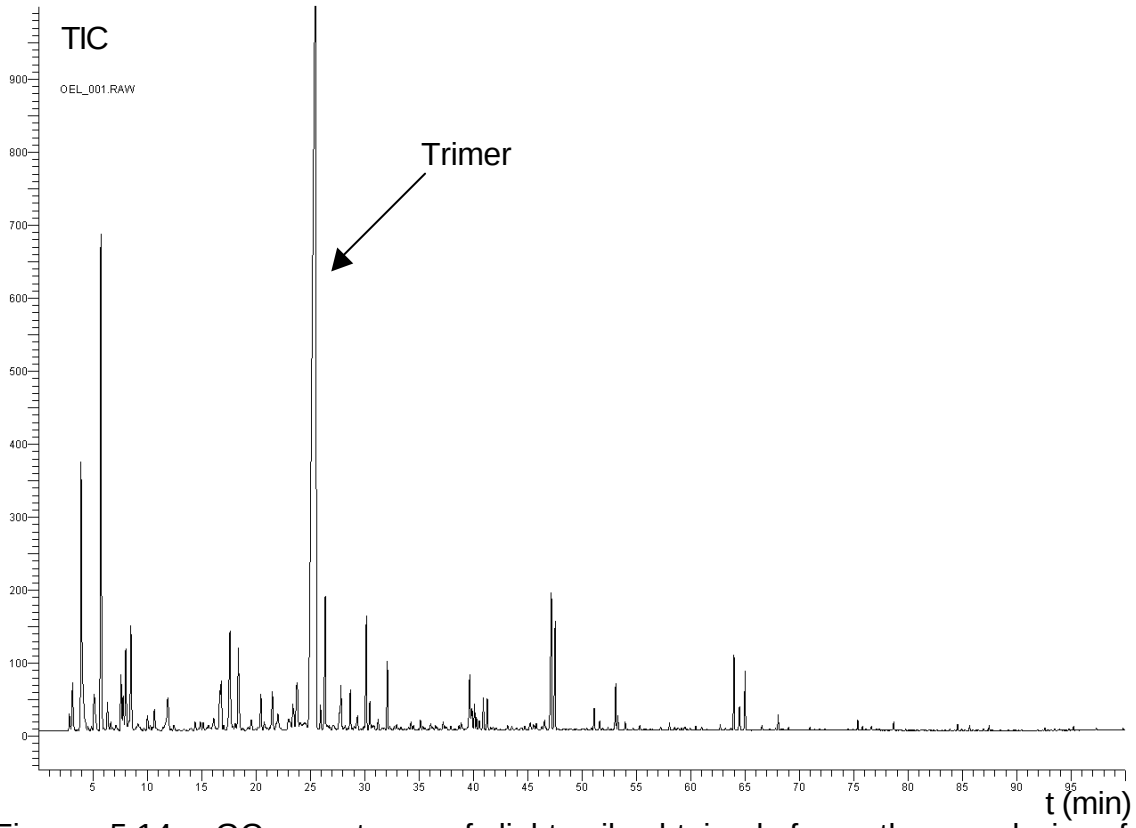


Figure 5.14.- GC spectrum of light oil obtained from the pyrolysis of polypropylene.

Table 5.3.- Main single product components of the pyrolysis of PP without catalysts

	WOC	
	400ºC	**500ºC**
Component (gas + light oil)		
Hydrogen	0,00	0,07
Methane	0,20	0,79
Ethane	0,56	1,89
Ethene	0,05	0,65
Propane	0,25	0,68
Propene	3,43	9,59
1-Butene	0,00	0,07
1,3-Butadiene	2,46	1,93
2-Methyl-propene	0,00	0,50
2-Butene	0,85	2,62
1-Pentene	0,07	0,27
2-Methyl-1-butene	0,00	0,14
2-Methyl-2-butene	0,41	3,67
2-Methyl-1-pentene	0,10	5,60
2-Methyl-2-hexene	0,00	0,72
2,4-Dimethyl-1-heptene	4,27	24,88
3-Methyl-3-undecene	0,33	1,48
7-Methyl-1-undecene	0,49	1,55
wt % heavy oil fraction	35,40	17,24

5.2.2.2. $TiCl_3$

$TiCl_3$ is a useful Ziegler-Natta catalyst for polymerization (see chapter 3.3). The idea was to use such catalyst also to depolymerise plastics in a thermal-catalytical reaction and to observe the influence of the catalyst in the degradation.

As mentioned in chapter 5.1.5, $TiCl_3$ is a solid and high reactive under oxygen atmosphere. For the experiments PP and the catalyst were mixed in a silo (chapter 5.1.1) using a glove box. The silo once the sample was prepared it was linked to the installation and the reactor was heated until the programmed temperature. Then the silo was opened and the PP and catalyst fell down simultaneously into the reactor where the pyrolysis reaction started.

5.2.2.2.1. Experimental conditions

The experimental conditions (table 5.4) were similar to the conditions of the non-catalytical reaction. Pyrolysis temperatures of 350 ºC, 400 ºC and 500 ºC were chosen and beside the input amount of PP, the amount of the catalyst was modifiable (0,1; 1,0 and 5,0 wt%).

Table 5.4.- Experimental parameters

Catalyst	wt % cat.	T (ºC)	Total input material (g)	wt % pyrolysed PP	wt % gas	wt % light oil fraction	wt % heavy oil fraction	wt % not pyrolysed PP
$TiCl_3$	0,10	400	10,00	91,19	10,36	61,20	19,63	8,81
		500	10,00	94,12	11,76	57,77	24,58	5,88
	1,00	400	10,00	88,83	5,04	68,66	15,13	11,17
		500	10,00	99,50	10,89	53,85	34,76	0,50
	5,00	400	10,00	91,79	3,53	75,52	12,73	8,21
		500	10,00	97,62	19,05	46,90	31,67	2,38

Experiments at 350 ºC didn't give any results and therefore the corresponding parameters are not listed.

5.2.2.2.2. Products

The products obtained have been compared with the results obtained in the non-catalytic pyrolysis. Figure 5.15 indicates the 3 fractions obtained in the pyrolysis reaction with and without catalysts. Figure 5.16 shows the different carbon number fractions obtained in the processes.

From the experiments the conclusion can be drawn that the input of $TiCl_3$ allows to run the reaction at lower temperatures. The amount of PP not pyrolysed was 42,15 wt% after one hour of reaction at 400 ºC. But the use of the catalyst led to a decrement down to 11,17 wt% (400 ºC and 1 wt% of catalyst).

The results of the reaction run with $TiCl_3$ at 400 ºC are equal and partially even better than the ones obtained in the pyrolysis reaction at 500 ºC without catalyst:

The amounts of light oil fractions are in both cases higher than 50 wt% (of the total mass introduced), and after running the reaction with 1 wt% and 5 wt% of $TiCl_3$ the amounts of light oil fractions were 68,66 wt% and 75,52 wt% respectively (and therewith higher than the yield of the non-catalytic reaction which was 62,21 wt%). Further, it is important to note that the gas amount obtained in each experiment with $TiCl_3$ was lower than the gas amount obtained in the reaction at 500 ºC without catalyst (table 5.4).

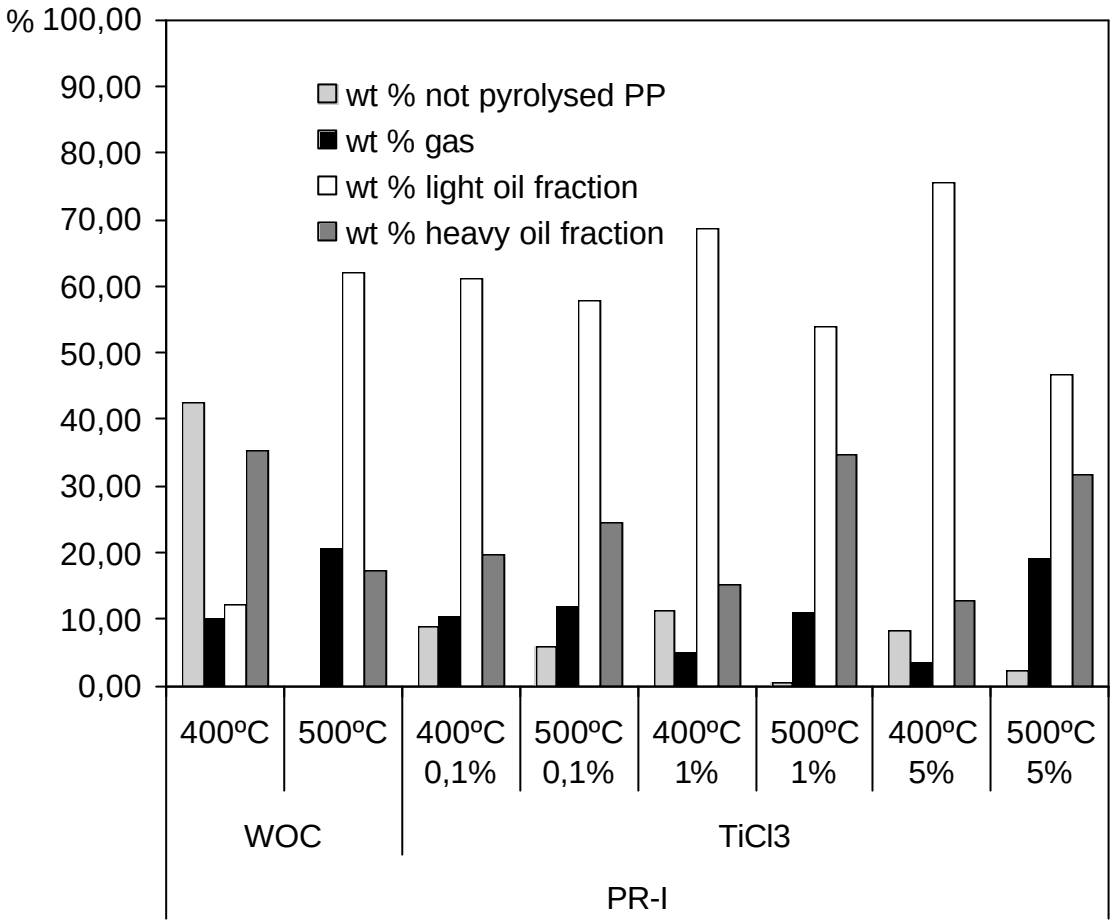


Figure 5.15.- Products distribution (wt %) of polypropylene's pyrolysis

The main components are listed in table 5.5. C9 was the main fraction produced in the reaction carried out at pyrolysis temperatures of 400 ºC and 500 ºC with $TiCl_3$ (0,1 wt%, 1 wt% and 5 wt%), which is shown in figure 5.16.

Further, it can be observed that the results of the catalytic reactions run at 400 ºC are better than the results obtained at 500 ºC (higher amounts of C9). The catalyst is more effective when the reaction is run at the lower temperature. An explanation for this effect can be found in the physical properties of $TiCl_3$. The melting point of such catalyst is 425 ºC and, if this temperature is overslepped, the catalyst decomposes and loses the catalytical properties. Additionally the subproducts of the decomposition could produce interferences in the depolymerisation reaction.

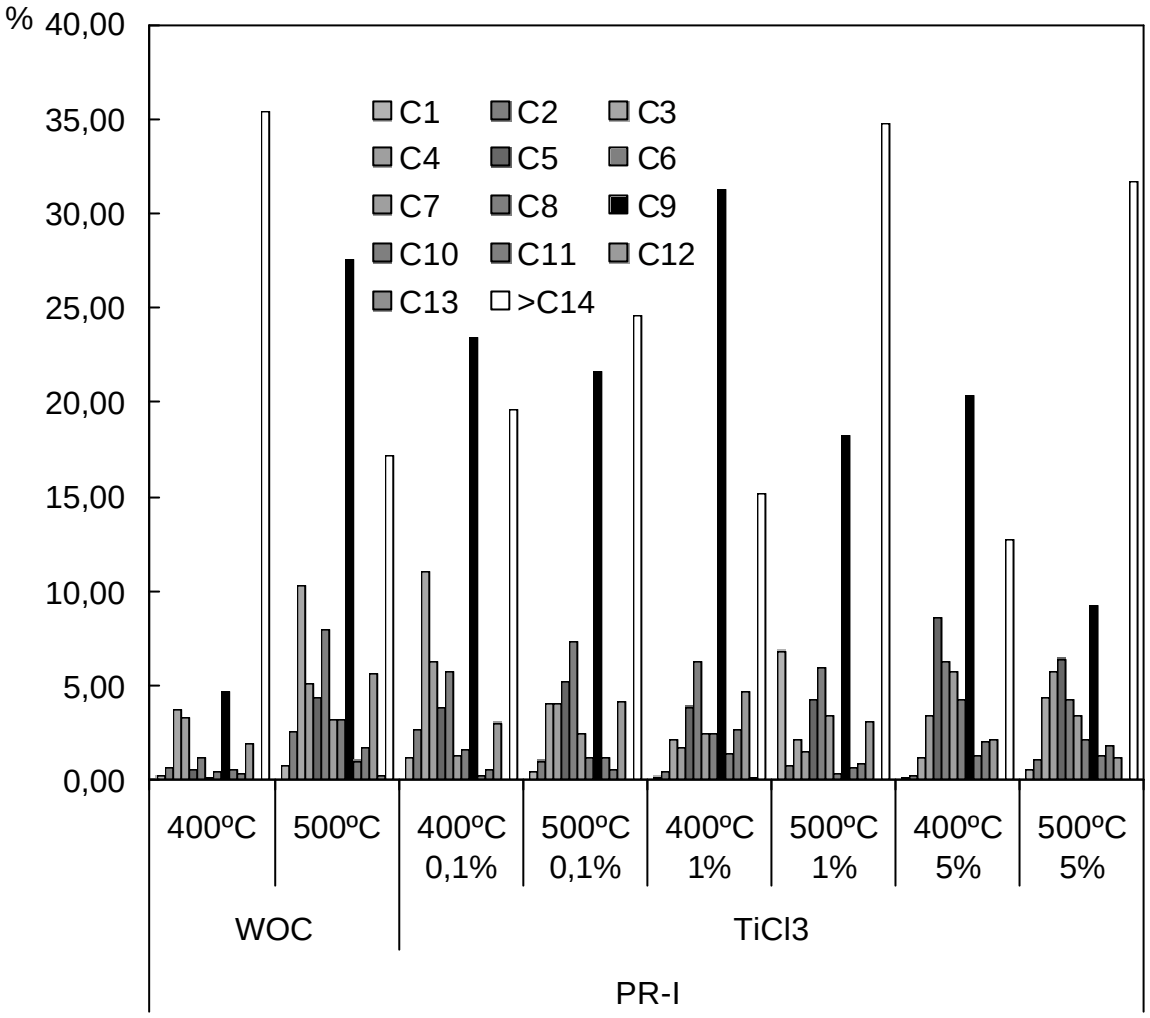


Figure 5.16.- Product fractions of polypropylene's pyrolysis

Processes with 5 wt% and 1 wt% of $TiCl_3$ produced at 500 ºC 31,67 wt% and 34,76 wt% of heavy oil fractions. When the temperature was reduce to 400 ºC the heavy oil fraction significantly sunk to 12,76 wt% by using 5 wt% of $TiCl_3$ and to 15,13 wt% by using 1 wt% of this catalyst. The amount of trimer (C9) increased (31,28 wt% with 1 wt% $TiCl_3$ and 20,41 wt% with 5 wt% $TiCl_3$).

Figure 5.17 shows the light oil chromatograms of the experiments run at a temperature of 400 ºC with different amounts of catalyst. The main peak corresponds to the trimer 2,4-Dimethyl-1-heptene.

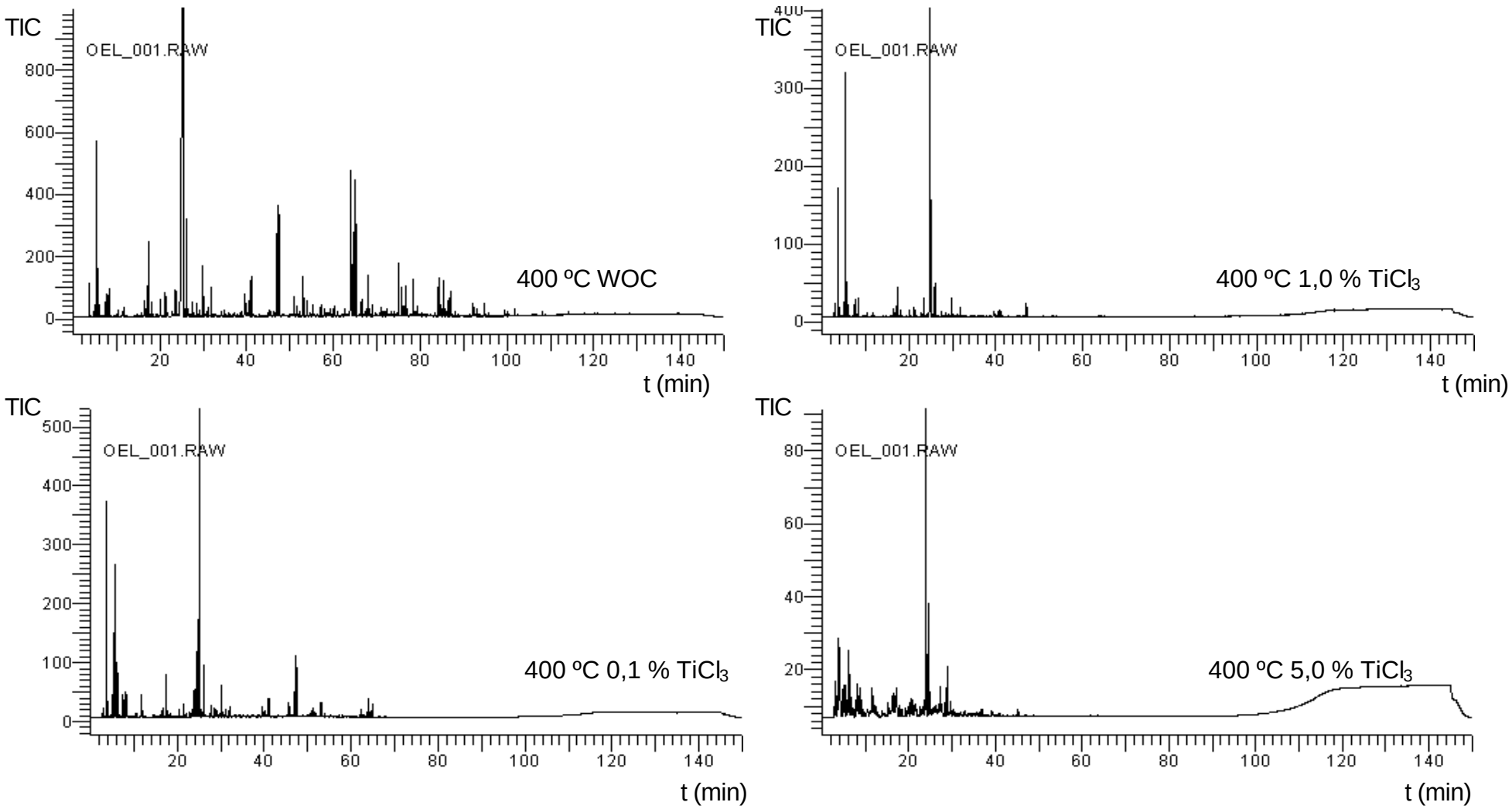


Figure 5.17.- Light oil chromatograms comparison

Table 5.5.- Main single product components of the pyrolysis of PP using $TiCl_3$ as catalyst

	$TiCl_3$					
	400ºC 0,1%	**500ºC 0,1%**	**400ºC 1%**	**500ºC 1%**	**400ºC 5%**	**500ºC 5%**
Component (gas + light oil)						
Hydrogen	0,00	0,05	0,04	0,19	0,21	0,23
Methane	1,18	0,41	0,17	6,84	0,08	0,56
Ethane	2,24	0,74	0,38	0,51	0,18	0,68
Ethene	0,39	0,27	0,06	0,22	0,05	0,43
Propane	0,81	0,33	0,23	0,22	0,13	0,89
Propene	10,29	3,74	1,85	1,88	1,09	3,49
1-Butene	2,20	0,06	0,04	0,01	0,02	1,99
1,3-Butadiene	0,00	1,97	0,86	0,23	0,47	0,36
2-Methyl-propene	0,23	0,69	0,19	0,64	1,17	0,19
2-Butene	3,79	1,35	0,59	0,57	1,69	3,22
1-Pentene	0,00	0,26	0,06	0,05	0,10	0,52
2-Methyl-1-butene	0,00	0,32	0,00	0,03	0,10	1,19
2-Methyl-2-butene	3,32	3,73	3,42	3,34	5,26	1,98
2-Methyl-1-pentene	4,94	5,39	4,09	3,65	1,95	1,17
2,3-Dimethyl-2-butene	0,30	0,33	1,03	0,70	2,30	1,55
2-Methyl-2-hexene	0,04	0,45	0,94	1,03	2,41	0,70
2,4-Dimethyl-1-heptene	21,83	19,72	23,51	16,94	16,21	6,55
2,3,7-Trimethyl-2-octene	0,00	0,01	0,23	0,02	0,06	0,21
3-Methyl-3-undecene	1,35	1,01	0,55	0,22	0,40	0,25
7-Methyl-1-undecene	0,50	1,63	2,32	1,12	0,07	0,06
wt % heavy oil fraction	19,63	24,58	15,13	34,76	12,73	31,67

5.2.2.3. $TiCl_4$

$TiCl_4$ is as $TiCl_3$ a catalyst frequently used in the polymerisation of PP. That is the reason why it was chosen for the experiments as well. The input of $TiCl_4$ should show the influence of the catalyst on the degradation reaction.

As $TiCl_4$ is liquid (chapter 5.1.6) it was not possible to prepare the sample in a glove box (figure 5.18) [91, 92] as done with $TiCl_3$. For this reason a modified silo was used in order to work with syringes injecting the catalyst direct into the silo and mixing it there with the PP.

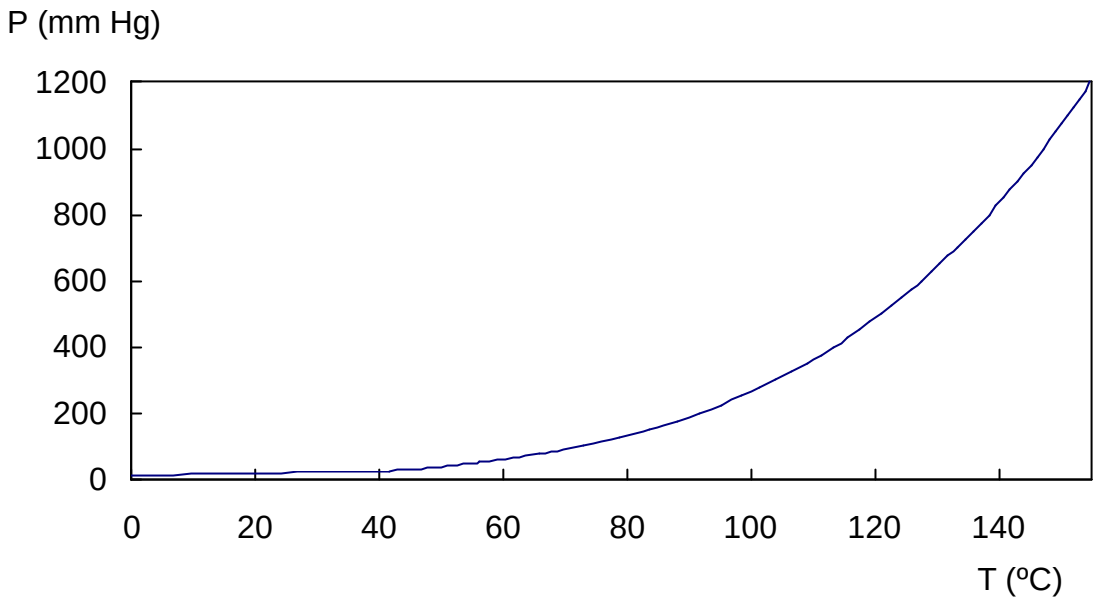


Figure 5.18.- Vapour pressure and boiling point of titanium tetrachloride

The mathematical equation of the vapour equilibrium corresponds with:

$$\log P = 6{,}79094 - \left[\frac{1348{,}56}{(T + 208{,}52)}\right]$$

in which;

P = Pressure in mm Hg
T = Temperature in ºC

5.2.2.3.1. Experimental conditions

To compare properly the results of the catalytical reactions and to observe the influence of $TiCl_4$ in the process, same conditions as before (pyrolysis temperatures and amounts of catalyst) were applied (Table 5.6).

Table 5.6.- Experimental parameters

Catalyst	wt % cat.	T (ºC)	Total input material (g)	wt % pyrolysed PP	wt % gas	wt % light oil fraction	wt % heavy oil fraction	wt % not pyrolysed PP
$TiCl_4$	0,10	400	10,00	94,77	5,42	77,02	12,33	5,23
		500	10,00	99,33	3,14	75,35	20,84	0,67
	1,00	400	10,00	95,07	7,51	68,34	19,21	4,93
		500	10,00	98,67	5,81	49,39	43,47	1,33
	5,00	400	10,00	95,26	7,20	55,08	32,97	4,74
		500	10,00	99,05	4,27	51,99	42,80	0,95

Experiments at 350 ºC didn't give any results and therefore those parameters are not listed.

5.2.2.3.2. Products

Products obtained in all experiments are similar but the proportion of the products differed. Main products obtained are shown in table 5.7.

Table 5.7.- Main single product components of the pyrolysis of PP using $TiCl_4$ as catalyst

	$TiCl_4$					
	400ºC 0,1%	500ºC 0,1%	400ºC 1%	500ºC 1%	400ºC 5%	500ºC 5%
Component (gas + light oil)						
Hydrogen	0,22	0,37	0,12	0,19	0,54	0,60
Methane	0,61	0,31	0,48	0,47	1,06	0,09
Ethane	0,56	0,32	0,54	0,43	0,67	0,08
Ethene	0,09	0,12	0,05	0,10	0,08	0,03
Propane	0,18	0,10	0,40	0,25	0,53	0,05
Propene	3,35	2,52	4,05	1,96	2,90	0,44
1-Butene	0,01	0,01	0,04	0,03	0,05	0,01
1,3-Butadiene	0,54	0,27	0,60	0,65	0,64	0,05
2-Methyl-propene	0,81	1,08	0,38	0,07	0,08	0,10
2-Butene	0,45	0,34	0,61	0,56	0,72	0,14
1-Pentene	0,00	0,13	2,23	0,91	0,22	0,01
2-Methyl-1-butene	0,26	0,03	0,06	0,07	0,09	0,01
2-Methyl-2-butene	5,28	5,42	9,60	3,19	7,20	7,73
2-Methyl-1-pentene	6,61	6,35	1,80	0,95	1,02	1,78
2,3-Dimethyl-2-butene	0,49	0,46	4,23	1,08	0,10	0,13
2-Methyl-2-hexene	0,42	0,47	0,33	0,20	0,07	0,44
2,4-Dimethyl-1-heptene	22,13	22,13	16,86	11,55	2,23	2,17
2,3,7-Trimethyl-2-octene	0,18	0,18	1,71	1,78	1,43	0,41

	$TiCl_4$					
	400ºC 0,1%	**500ºC 0,1%**	**400ºC 1%**	**500ºC 1%**	**400ºC 5%**	**500ºC 5%**
Component (gas + light oil)						
3-Methyl-3-undecene	1,96	1,53	1,48	0,77	0,77	0,04
7-Methyl-1-undecene	2,76	2,53	1,19	0,90	0,11	0,33
wt % heavy oil fraction	12,33	20,84	19,21	43,47	32,97	42,80

After carrying out the reaction at 400 ºC for one hour PP was largely pyrolysed (figure 5.19). The leftover of PP not pyrolysed at 400 ºC with 0,1 wt% of the catalyst was 5,23 wt% and therewith the highest residue compared with results obtained in reactions which were run with higher amounts of catalyst.

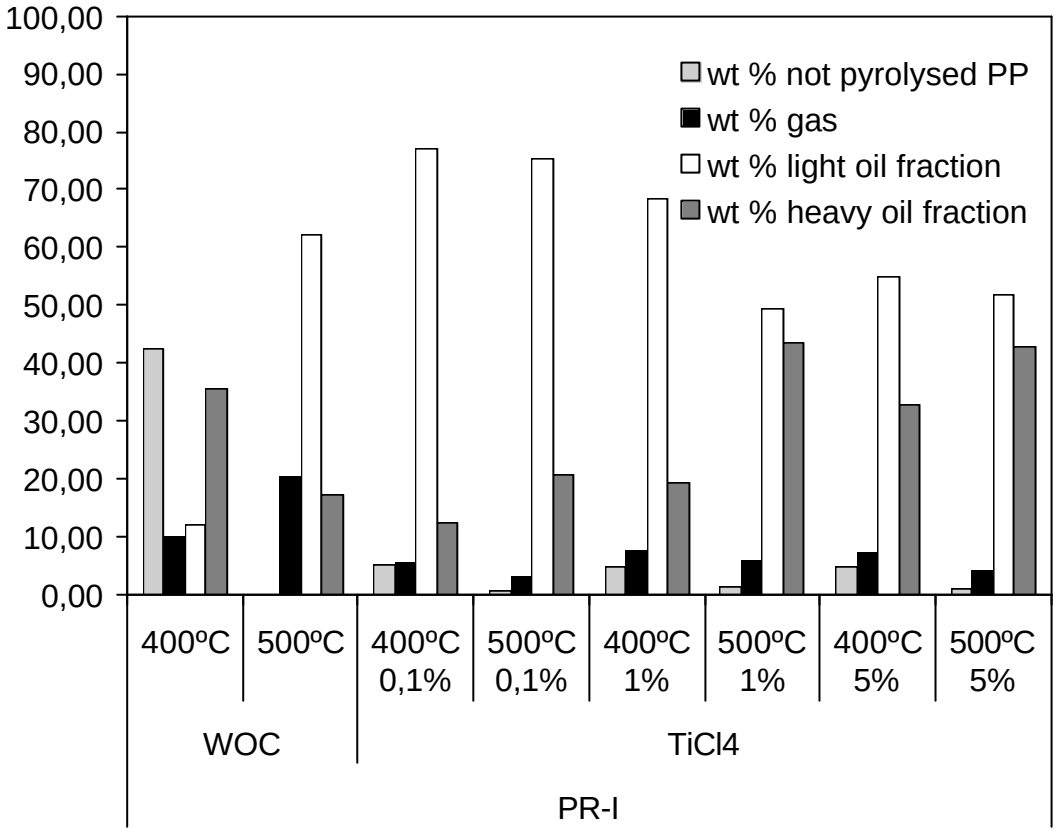


Figure 5.19.- Products distribution (wt %) of polypropylene's pyrolysis

As expected, when the reaction was run at 500 ºC and with $TiCl_4$ the leftover of PP not pyrolysed was very small. All values were not higher than 1,5 wt% (0,67 wt%, 1,33 wt% and 0,95 wt% for 0,1 wt%, 1,0 wt% and 5,0 wt% of catalyst respectively). Figure 5.19 indicates that the main fraction was always the light

oil fraction. But the highest yield of light oil was produced in the reaction run at a temperature of 400 ºC and with 0,1 wt% of catalyst (77 wt% of light oil) as well as at 500 ºC and with 0,1 wt% of catalyst. After running the reaction at 400 ºC and with 1 wt% of $TiCl_4$, 68,34 wt% of light oil fractions could be produced. Using amounts of catalyst over 1 wt% the light oil yield was still the main fraction (55 wt% at 400 ºC and 52 wt% at 500 ºC with 5 wt% catalyst), but the heavy oil fraction yield increased to values of 33 wt% and 43 wt% at 400 ºC and 500 ºC respectively.

In all cases the gas production was insignificant (lower values than 7,5 wt%) compared with the production at 500 ºC under non catalytical conditions (20,56 wt%).

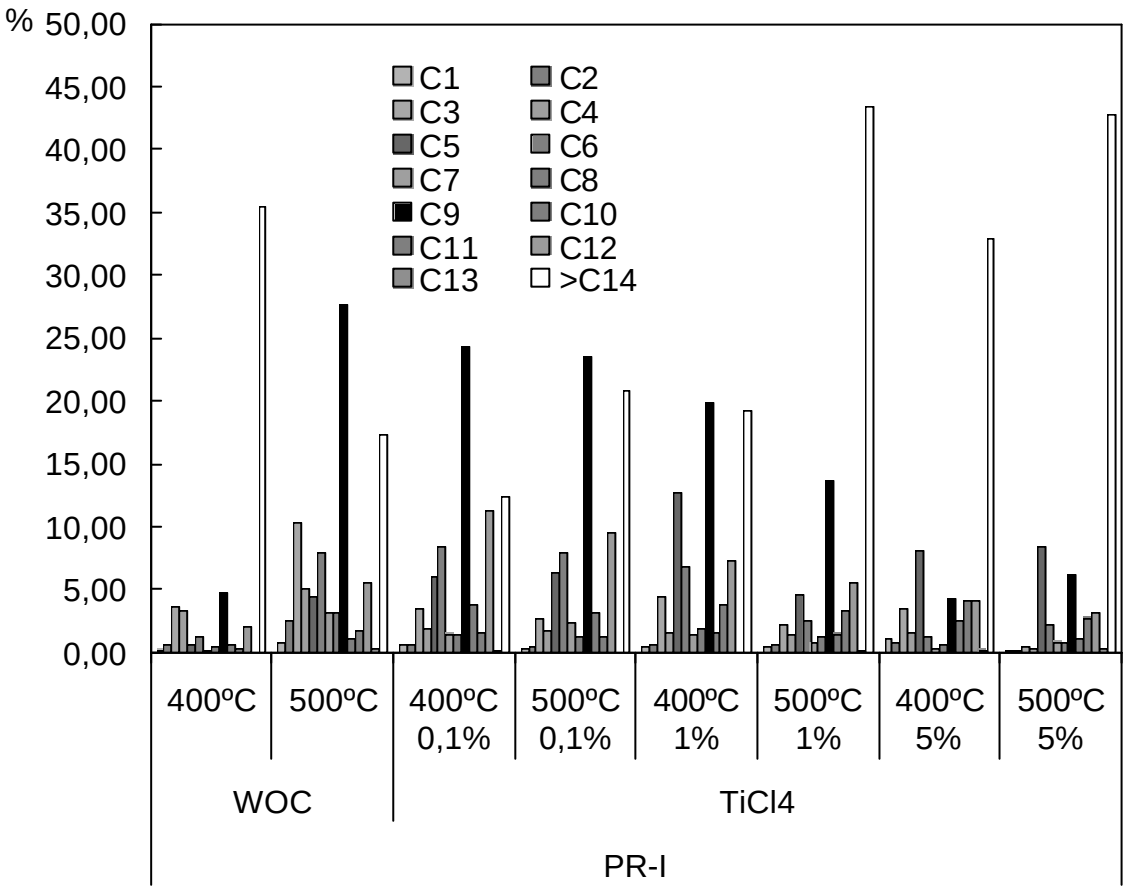


Figure 5.20.- Product fractions of polypropylene's pyrolysis

Figure 45.20 shows that when low amounts of the catalyst, (between 0,1 wt% and 1,0 wt%) were used, the C9 fraction with the trimer molecule was most

produced. But when the proportion of catalyst used was increased to 5 %, the trimer production decreased dramatically in benefit of fractions longer than C13. The figure shows this trend clearly. All the other fractions are not higher than 10 %.

Figure 5.21, shows all the light oil fraction chromatograms and indicates very well the decrease of the trimer running the experiments at 400 ºC and 500 ºC and using 5 % of the catalyst.

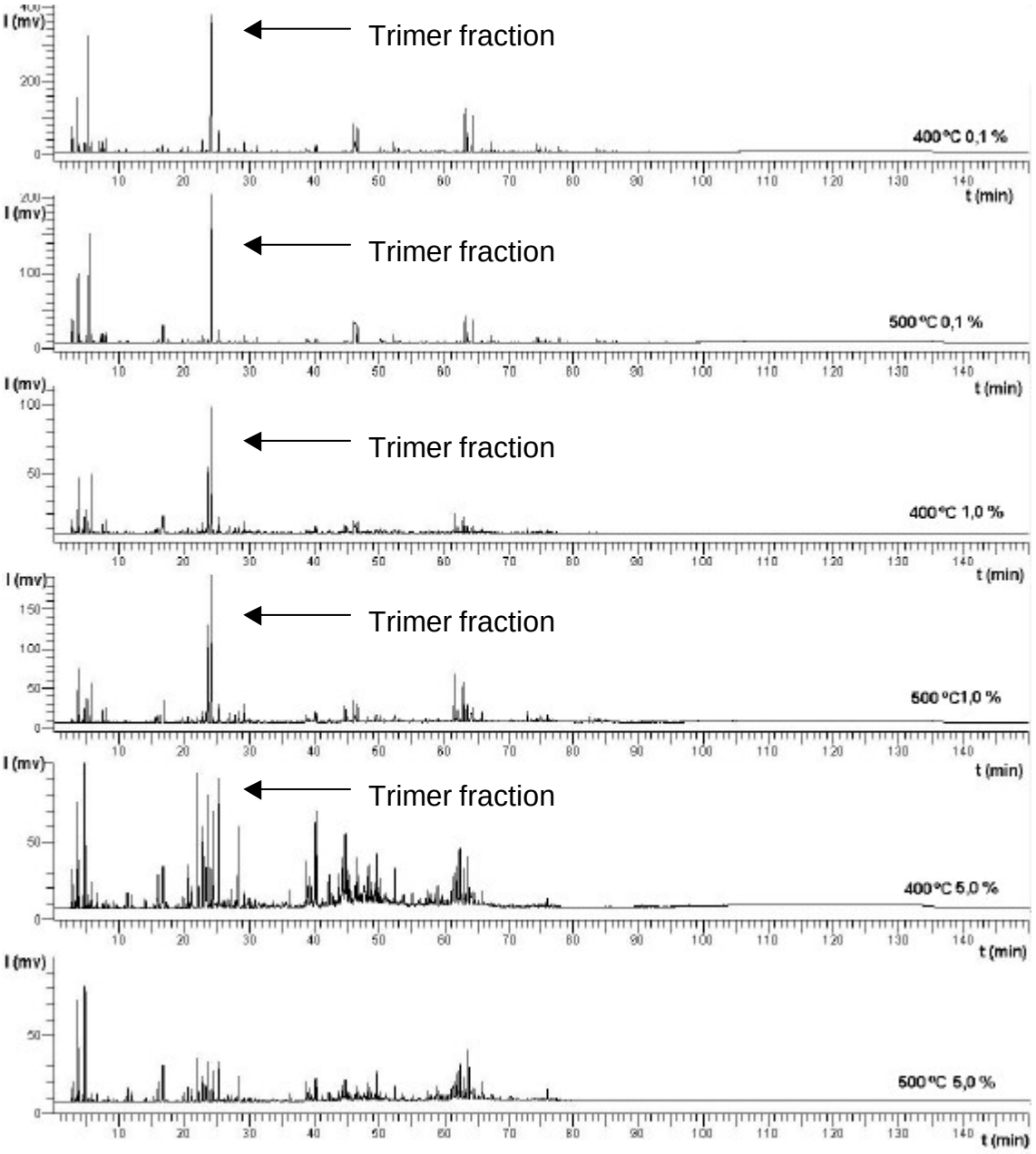


Figure 5.21.- Light oil chromatograms of $TiCl_4$ experiments

5.2.2.4. $AlCl_3$

As it is described in chapter 5.1.6, $AlCl_3$ is a Lewis acid, an electron acceptor used in the catalytic cracking [93]. It can abstract electrons from alkenes forming a carbocation (+). In this strongly acid system the process of ionic degradation are intensified as well as the isomerisation of the products [94].

5.2.2.4.1. Experimental conditions

As it could be observed that it is possible to run the pyrolysis reaction with $AlCl_3$ at 300 ºC obtaining pyrolysis products, the scale of experiments with this catalyst was expanded.

At the end, 11 experiments were carried out with $AlCl_3$ as catalyst. This time, the pyrolysis temperature scale began with 250 ºC as products still could be obtained at 300 ºC. It should be investigated, if there is also the possibility to pyrolyse at temperatures lower than 300 ºC.

The temperature conditions and catalyst ratios used are represented in table 5.8.

Table 5.8.- Experimental parameters

Catalyst	wt % cat.	T (ºC)	Total input material (g)	wt % pyrolysed PP	wt % gas	wt % light oil fraction	wt % heavy oil fraction	wt % not pyrolysed PP
$AlCl_3$	0,10	300	10,00	3,60	0,70	0,87	2,03	96,40
		400	10,00	95,50	2,20	72,47	20,83	4,50
		500	10,00	99,40	4,40	62,65	32,36	0,60
	1,00	250	10,00	8,12	3,86	1,28	2,98	91,88
		300	10,00	68,42	0,69	55,83	11,90	31,58
		400	10,00	96,44	9,21	80,10	7,13	3,56
		500	10,00	97,82	7,43	76,51	13,88	2,18
	5,00	250	10,00	30,58	16,81	4,13	9,64	69,42
		300	10,00	76,35	15,57	41,72	19,06	23,65
		400	10,00	98,48	10,35	76,39	11,73	1,52
		500	10,00	96,11	7,03	68,15	20,93	3,89

5.2.2.4.2. Products

It turned out that the minimum temperature at which PP could be pyrolysed in a reaction with only 0,10 wt% of $AlCl_3$ was 300 ºC. But after increasing the catalyst amount up to 5 wt%, pyrolysis products were also obtained at a temperature of 250 ºC as figure 5.22 shows.

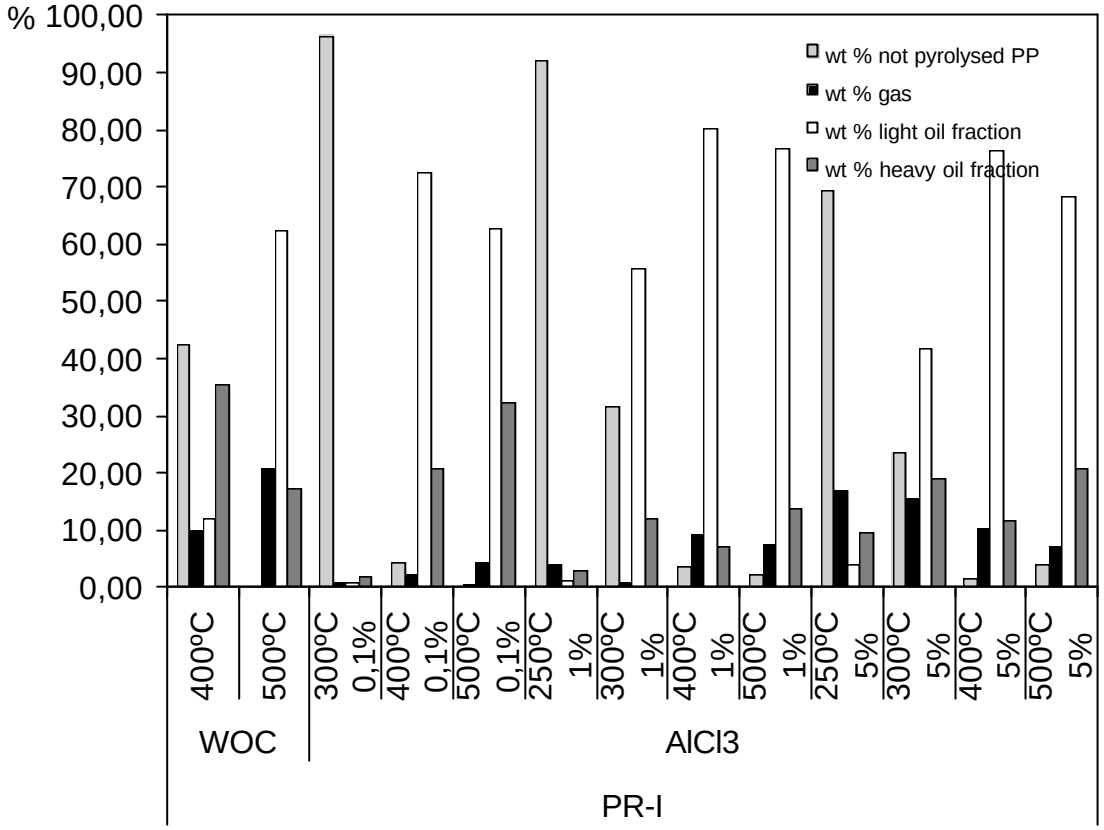


Figure 5.22.- Products distribution (wt %) of polypropylene's pyrolysis

As $AlCl_3$ is a solid like $TiCl_3$, the sample preparations were similar. PP and the catalyst were mixed under inert conditions in a silo using a glove box. Then the properly closed silo was linked to the rest of the reactor's system. The pyrolysis installation was filled with nitrogen gas and once the reaction temperature was achieved the silo was opened. The experiments were conducted in all cases during one hour from the moment on the silo's valve was opened.

Figure 5.22 shows in a visual way the products obtained. When the reaction was run with low amounts of catalyst (0,1 wt%) at 300 ºC, 96,40 wt% of the PP

was not pyrolysed. But by increasing the catalyst amount to 1 % of the total sample weight, the not pyrolysed PP amount decreased to 31,58 wt%, and with a catalyst amount of 5 wt% to 23,65 wt%. When the reaction was carried out 250 ºC, something similar occurred. With amounts of 0,1 wt% of the catalyst, no products could be obtained (100 wt% not pyrolysed PP). The values of not pyrolysed PP decreased to 91,88 wt% and 69,42 wt% when 1 wt% and 5 wt% of catalyst respectively was used.

Regarding the fractions obtained, the light oil fraction (gasoline fraction) was the most produced in all experiments. Fractions close to 80 wt% could be obtained by running the reaction at 400 ºC and introducing amounts of catalyst of 1 wt% and 5 wt%. At 300 ºC, the light oil fraction was prime fraction (except for the pyrolysis with 0,1 wt% of catalyst). With 1 wt% of $AlCl_3$ 55 wt% of light oil could be produced and with 5 wt% 42 wt%. Regarding the gas fraction, interesting results could be obtained with amounts of 5 wt% of $AlCl_3$ (between 7 wt% and 16 wt%).

Figure 5.23 shows the product fractions depending on the carbon atom number of the chain. The results obtained with lower amounts of catalyst are quiet similar to those obtained in reactions with $TiCl_3$ and $TiCl_4$. This means that the most important fraction at 400 ºC and 500 ºC is the C9 fraction with amounts of 24 wt% and 21 wt% respectively; 22 wt% and 20 wt% corresponded to the trimer fraction. Table 5.9 shows the amounts of trimer.

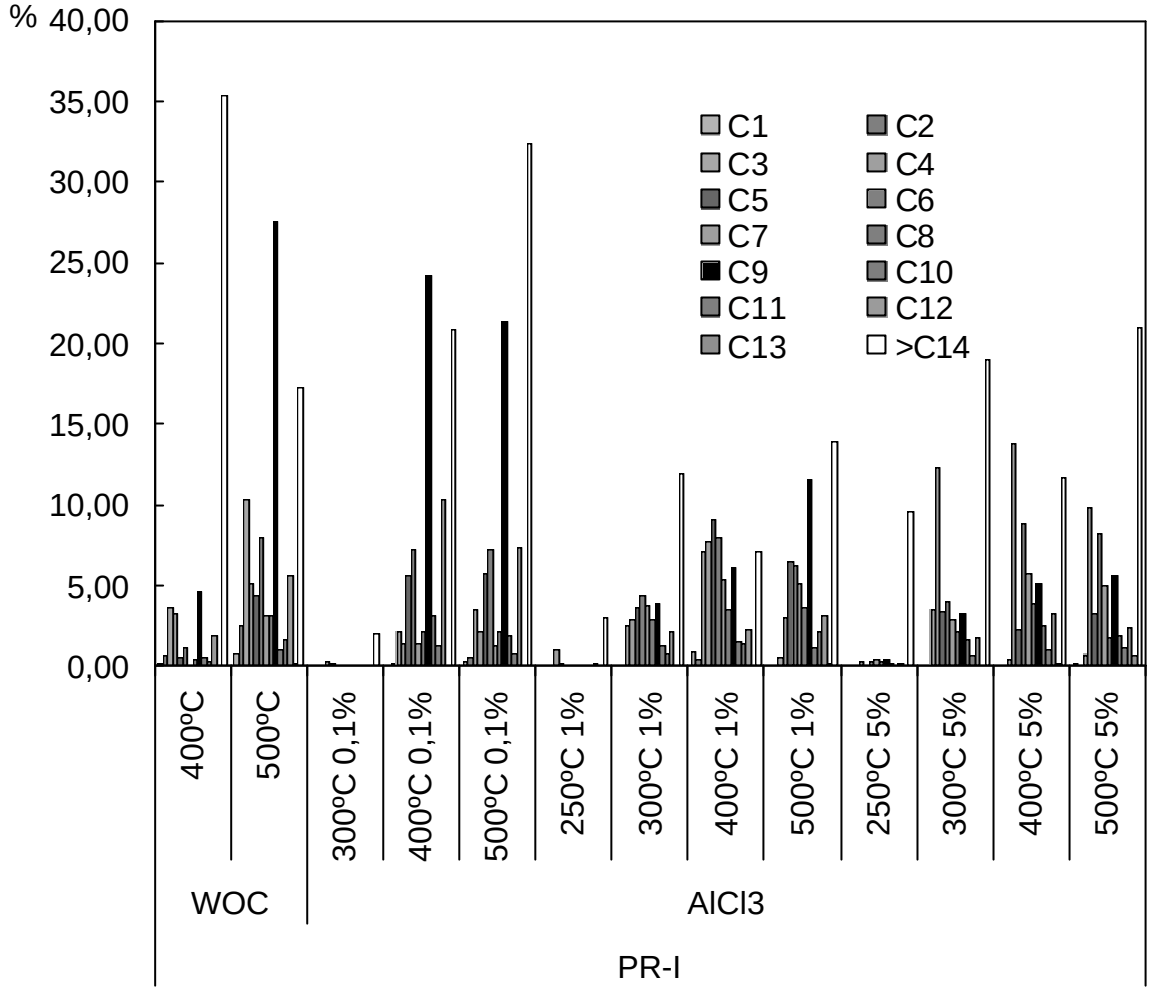


Figure 5.23.- Product fractions of polypropylene's pyrolysis

When the pyrolysis reaction was run with amounts of catalyst higher than 0,1 %, there was a totally different distribution of the products. The C9 fraction amount decreased dramatically. Figure 5.24 shows the chromatograms of the main experiments. The reference peak (trimer) does not excel anymore. The conclusion obtained from this figure is that by using amounts over 1% of $AlCl_3$ as catalyst the reactions selectivity decreases and the number of new products increases. But all new products don't exceed individually 1% from the total system mass balance. The other, well known fractions only are represented with amounts between 6 wt% and 10 wt%.

Table 5.9.- Main single product components of the pyrolysis of PP using $AlCl_3$ as catalyst

	$AlCl_3$										
	300ºC 0,1%	**400ºC 0,1%**	**500ºC 0,1%**	**250ºC 1%**	**300ºC 1%**	**400ºC 1%**	**500ºC 1%**	**250ºC 5%**	**300ºC 5%**	**400ºC 5%**	**500ºC 5%**
Component (gas + light oil)											
Hydrogene	0,00	0,05	0,20	0,00	0,25	0,90	0,65	0.96	0,01	0,74	5,64
Methane	0,00	0,10	0,35	0,00	0,02	0,92	0,07	0,00	0,04	0,04	0,21
Ethane	0,02	0,16	0,38	0,00	0,01	0,33	0,03	0,00	0,04	0,01	0,04
Ethene	0,00	0,02	0,11	0,00	0,00	0,11	0,01	0,00	0,03	0,00	0,03
Propane	0,01	0,07	0,16	0,04	0,02	0,40	0,02	0,01	0,32	0,02	0,05
Propene	0,10	2,03	3,42	0,04	2,52	6,66	0,56	0,01	3,22	0,43	0,67
1-Butene	0,03	0,01	0,01	1,00	0,16	1,23	0,01	0,19	5,41	0,23	0,52
1,3-Butadiene	0,23	0,37	0,55	0,01	0,01	0,51	0,02	0,15	3,35	0,12	0,01
2-Methyl-propene	0,00	0,03	0,06	0,00	0,49	1,55	0,46	0,00	0,09	4,78	2,81
2-Butene	0,05	0,97	1,49	0,04	2,29	4,39	2,55	0,03	3,46	8,72	6,55
1-Pentene	0,02	0,03	0,05	0,02	0,01	0,15	0,00	0,00	0,18	0,01	0,01
2-Methyl-1-butene	0,01	0,01	0,02	0,06	0,03	0,36	0,00	0,01	0,38	0,01	0,02
2-Methyl-2-butene	0,08	5,17	4,94	0,12	3,03	7,56	5,76	0,02	2,61	1,82	2,49
2-Methyl-1-pentene	0,02	5,60	5,16	0,02	2,00	3,41	2,06	0,25	3,54	7,45	6,53
2,3-Dimethyl-2-butene	0,00	0,44	0,60	0,00	0,97	2,55	2,57	0,01	0,00	0,49	0,62
2-Methyl-2-hexene	0,00	0,39	0,53	0,01	1,77	2,35	2,15	0,21	1,48	2,95	2,62
2,4-Dimethyl-1-heptene	0,02	22,44	19,94	0,03	1,55	3,57	7,47	0,24	1,65	2,58	3,05
2,3,7-Trimethyl-2-octene	0,01	0,18	0,13	0,02	0,14	0,24	0,73	0,02	0,09	0,17	0,19
3-Methyl-3-undecene	0,02	1,59	1,17	0,03	0,10	0,42	0,54	0,02	0,23	0,49	0,55
7-Methyl-1-undecene	0,00	2,47	2,12	0,00	0,14	0,15	0,66	0,02	0,18	0,29	0,08
wt % not pyrolysed PP	96,40	4,50	0,60	91,88	31,58	3,56	2,18	69,42	23,65	1,52	3,89

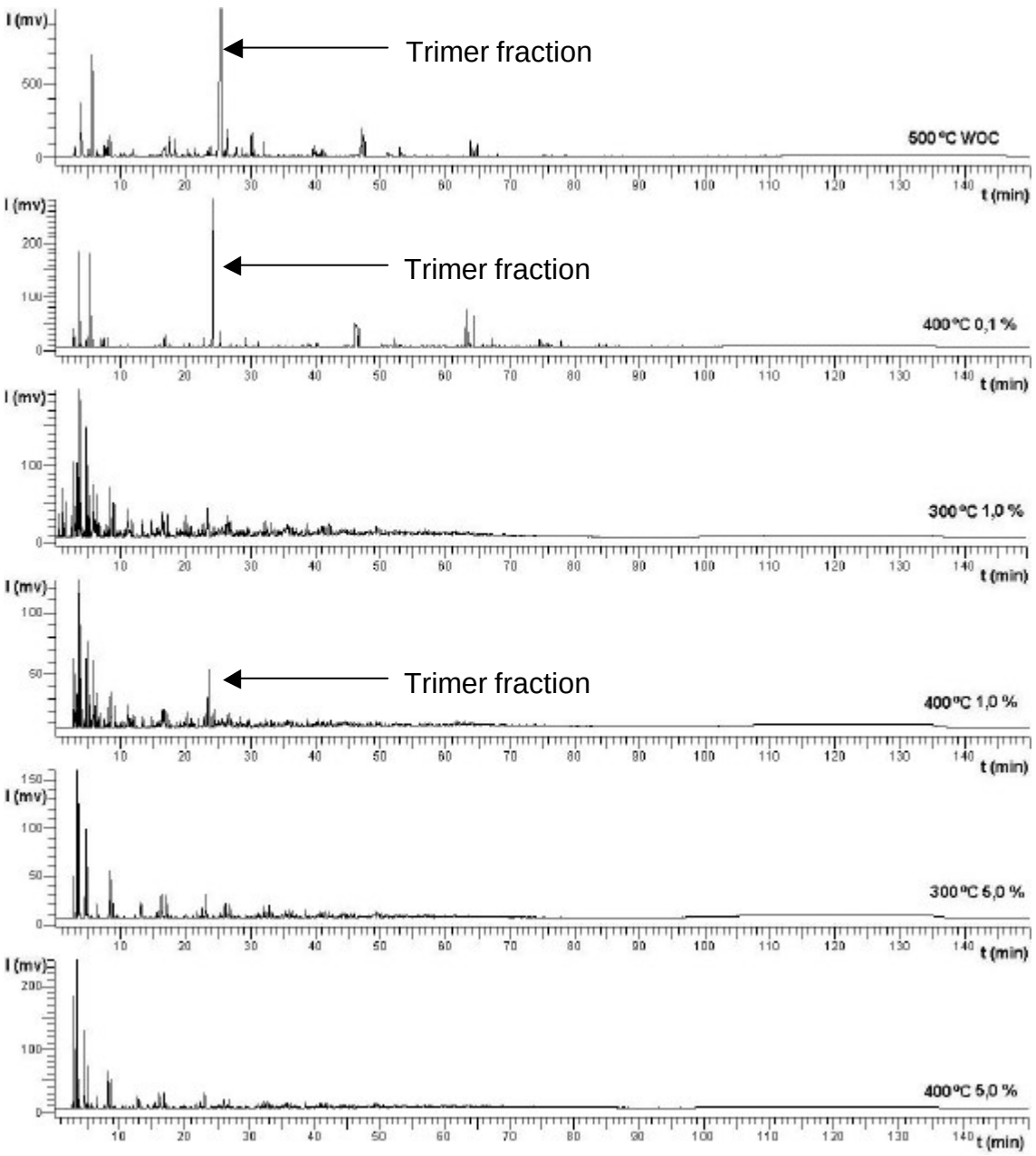


Figure 5.24.- Light oil chromatograms of $AlCl_3$ experiments

Figure 5.24 also shows the light oil fraction chromatogram for 500 ºC under non catalytical conditions. The Chromatogram of the experiment run with 0,1 wt% catalyst at 400 ºC shows a similar product distribution. Higher amounts of light oil hydrocarbons were obtained in the reaction with 1 wt% of the catalyst (the peaks concentration is at the beginning of the reaction the highest).

5.2.2.5. $AlCl_3$ + $TiCl_4$

The use of mixture catalyst systems is investigated for the polymerisation [11, 13, 95-97]. Here, experiments were carried out with a combination of $TiCl_4$ and $AlCl_3$, a catalyst system which is very similar to a Ziegler-Natta catalyst. There was the vague assumption that this combination could even increase the degradation of polypropylene under same conditions.

$TiCl_4$ and $AlCl_3$, were chosen because of the results obtained in reactions separately with these catalysts.

5.2.2.5.1. Experimental conditions

The mixtures of catalyst were prepared in different ratios. The experimental conditions were similar (temperatures and amounts of catalyst) to those of the preceding experiments. But one new variable was added, the $TiCl_4$:$AlCl_3$ catalyst's ratio. Table 5.10, indicates the experiments conducted and the conditions applied. Mass ratios of 1:1, 1:5 and 5:1 of $TiCl_4$:$AlCl_3$ were used in the experiments to observe the influence of each catalyst in each ratio.

Table 5.10.- Experimental parameters

Catalyst		wt % cat.	T (ºC)	Total input material (g)	wt % pyrolysed PP	wt % gas	wt % light oil fraction	wt % heavy oil fraction	wt % not pyrolysed PP
$TiCl_4$:$AlCl_3$	1:1	5,00	250	10,00	20,70	0,57	15,27	4,86	79,30
			300	10,00	88,98	26,12	47,07	15,80	11,02
			400	10,00	89,93	24,79	60,81	4,34	10,07
	1:5	1,00	300	10,00	24,26	7,62	4,99	11,64	75,74
		5,00	250	10,00	36,09	9,59	21,11	5,39	63,91
			300	10,00	49,67	0,09	47,25	2,32	50,33
	5:1	5,00	250	10,00	15,29	0,38	11,18	3,73	84,71
			300	10,00	38,94	2,37	20,00	16,56	61,06

It turned out that experiments with amounts of 1 wt% of catalyst in ratios 5:1 and 1:1 didn't provide products. Table 5.10 only refers to successful experiments.

The highest reaction temperature used in the experiments was 400 ºC. At this temperature the reaction was carried out with the catalysts of 5 wt% in the ratio 1:1. The other experiments were conducted at 300 ºC and at lower temperatures.

5.2.2.5.2. Products

At 300°C best results were obtained with 5 wt% of $TiCl_4$:$AlCl_3$ in a ratio of 1:1 (figure 5.25). In the reaction run at this temperature with catalysts ratios of 5:1 and 1:5 polypropylene was not pyrolysed (still 61 wt% and 50 wt% respectively of polypropylene in the reactor after 1 hour of reaction time). But when the reaction was run with the catalysts in the ratio of 1:1, an amount of 47 wt% of light oil fraction and 25 wt% of gas was obtained. 11 wt% of polypropylene not pyrolysed was still left after a one hour reaction in the batch reactor. C3 (propene) and C4 (2-Butene) were the most important fractions (with 9 wt% and 11 wt% respectively) (figure 5.26).

This shows that the combination of $TiCl_4$/$AlCl_3$ in the ratio 1:1 is the most effective catalyst in the depolymerisation of polypropylene at 300 °C. Only 11 wt% of PP was not pyrolysed. This is a very good result compared with results obtained in the reaction with 5 wt% $AlCl_3$ (25 wt%) and in the reaction without catalyst (almost 100 wt%). When the ratio of $TiCl_4$:$AlCl_3$ was 5:1 or 1:5, the degradation was much slower. This is recognizable by looking at the values of not pyrolysed PP.

After a one hour reaction with a 1:1 ratio and 5 wt% of catalyst at 400 °C, the amount of not pyrolysed polypropylene was even lower than 10 wt%, the gas amount was 25 wt% and 61 wt% of the light oil fraction was obtained.

Regarding the gas and the light oil fraction, the highest fraction obtained was C4 (14,5 wt%, 2-Butene) followed by the C5 fraction (11 wt%, 2-Methyl-2-butene (table 5.11).

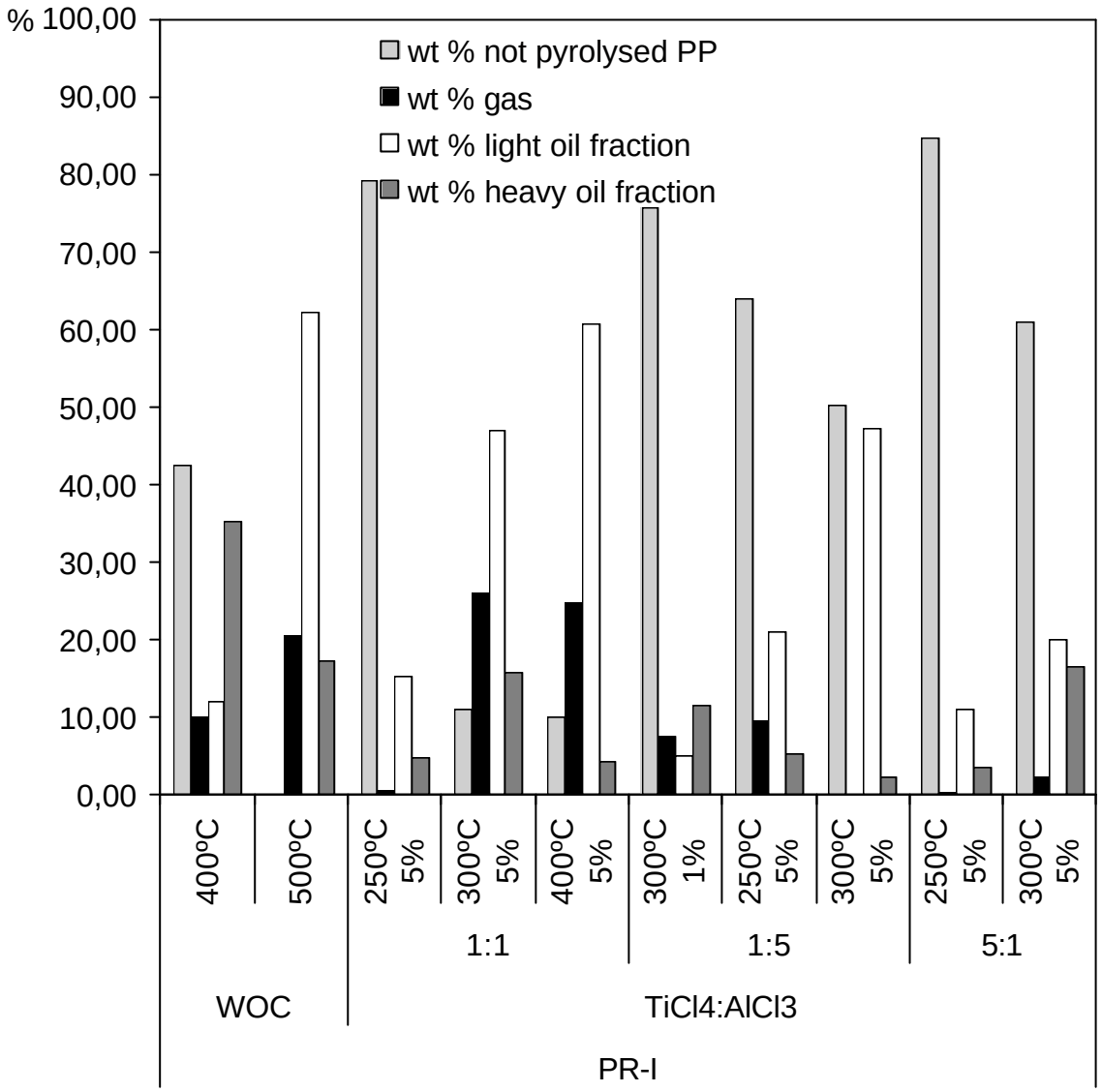


Figure 5.25.- Products distribution (wt %) of polypropylene's pyrolysis

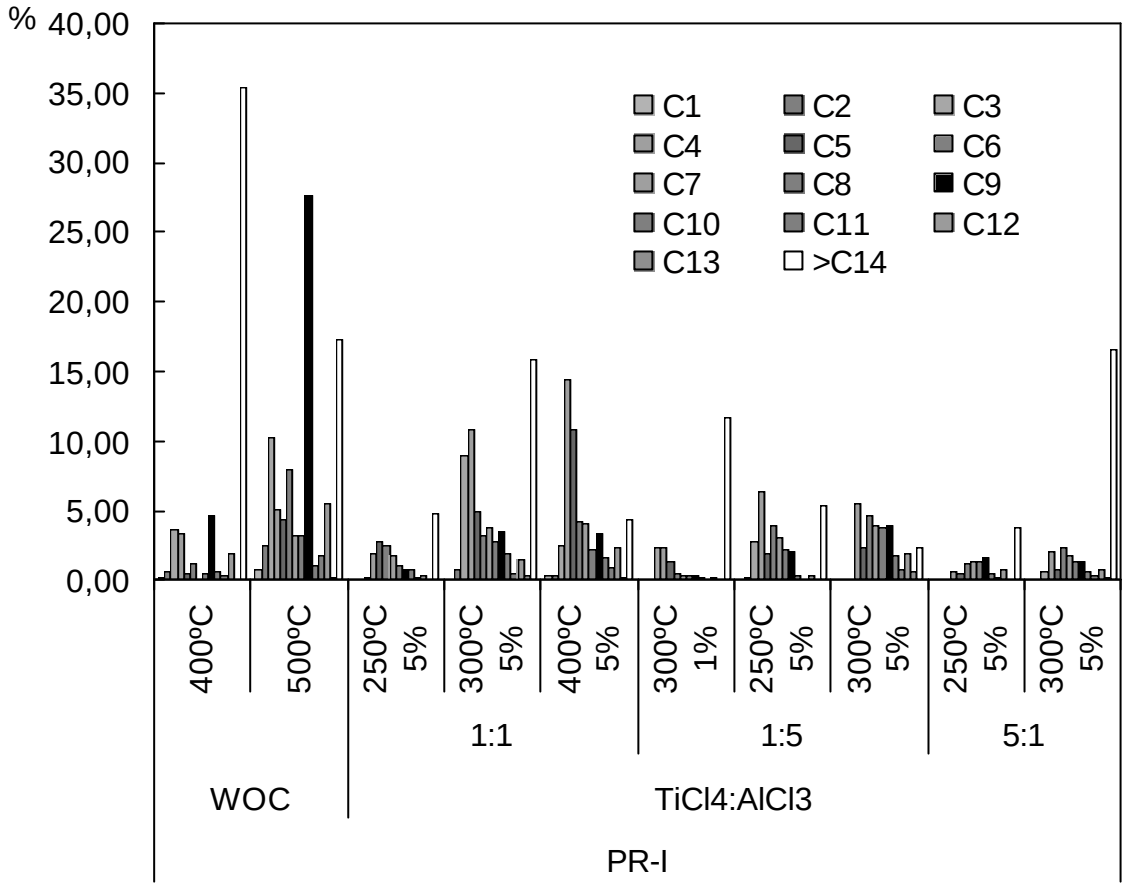


Figure 5.26.- Product fractions of polypropylene's pyrolysis

Table 5.11.- Main single product components of the pyrolysis of PP using $TiCl_4$:$AlCl_3$ mixtures as catalyst

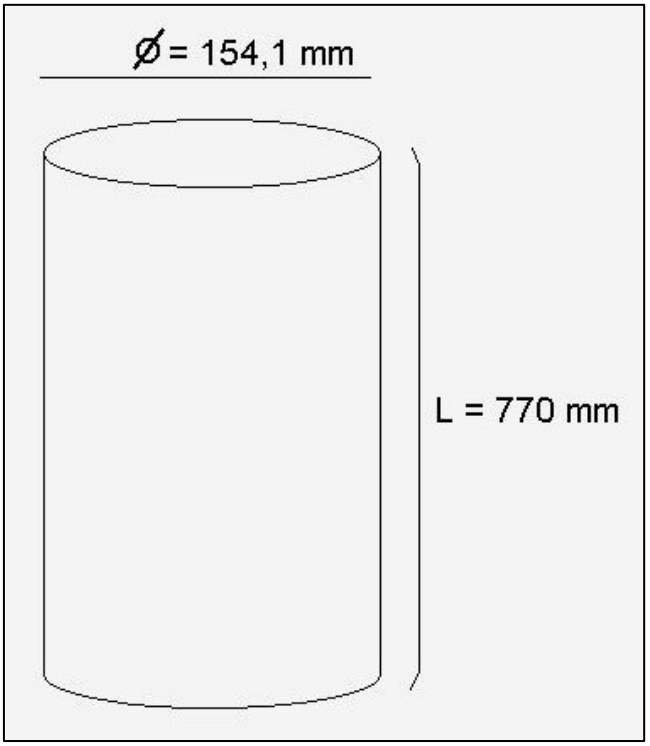
	$TiCl_4$:$AlCl_3$							
	1:1			**1:5**			**5:1**	
	250ºC 5%	**300ºC 5%**	**400ºC 5%**	**300ºC 1%**	**250ºC 5%**	**300ºC 5%**	**250ºC 5%**	**300ºC 5%**
Component (gas + light oil)								
Hydrogene	0,00	0,05	0,11	0,00	0,00	0,03	0,00	0,00
Methane	0,00	0,12	0,28	0,00	0,02	0,00	0,00	0,01
Ethane	0,00	0,09	0,26	0,01	0,02	0,00	0,00	0,01
Ethene	0,01	0,63	0,09	0,08	0,13	0,00	0,01	0,04
Propane	0,00	1,14	0,63	0,14	0,04	0,00	0,00	0,06
Propene	0,20	7,91	1,87	2,20	2,73	0,05	0,12	0,59
1-Butene	0,01	0,36	4,57	0,08	0,10	0,00	0,00	0,02
1,3-Butadiene	0,00	0,32	3,15	0,06	0,02	0,00	0,00	0,09
2-Methyl-propene	0,09	1,36	1,59	0,05	0,50	1,30	0,05	0,19
2-Butene	1,83	8,86	5,12	2,17	5,73	4,15	0,61	1,85
1-Pentene	0,00	0,04	0,58	0,02	0,03	0,00	0,00	0,00
2-Methyl-1-butene	0,05	1,42	1,79	0,65	1,03	0,01	0,04	0,19
2-Methyl-2-butene	1,67	1,39	7,16	0,19	0,23	1,67	0,11	0,48
2-Methyl-1-pentene	1,76	2,32	2,60	0,33	3,44	3,92	0,80	1,73
2,3-Dimethyl-2-butene	0,06	0,16	0,59	0,02	0,05	0,14	0,06	0,11
2-Methyl-2-hexene	0,90	1,93	2,46	0,19	1,47	1,93	0,66	0,91
2,4-Dimethyl-1-heptene	0,47	1,58	1,69	0,16	1,11	2,00	0,71	0,64
2,3,4-Trimethylhexane	0,02	0,00	0,10	0,01	0,00	0,01	0,03	0,01
2,3,7-Trimethyl-2-octene	0,06	0,00	0,12	0,00	0,00	0,10	0,00	0,01
3-Methyl-3-undecene	0,06	0,29	0,43	0,03	0,14	0,27	0,12	0,19
7-Methyl-1-undecene	0,00	0,13	0,10	0,03	0,01	0,22	0,10	0,09
wt % heavy oil fraction	4,86	15,80	4,34	11,64	5,39	2,32	3,73	16,56

5.2.3. LWS-V

8 experiments were carried out in the fluidised bed reactor LWS-V (figure 5.2), shown in table 5.12. To run the experiments in the fluidised bed reactor required much more time than the work with the PR-I reactor as the preparation, the construction, the dismount and the cleaning was costlier.

For this reason only the favourable experimental conditions, known from the experiments run in the PR-I reactor were applied in LWS-V.

It has to be mentioned that the working conditions of such a reactor are different from the conditions of a batch reactor. In PR-I, the reaction time was one hour; the residence time was variable. For example, the reaction could have been run for a few milliseconds or 3600 seconds. The residence time of the products for the experiments carried out in the LWS-V reactor was always constant:



$V = B \times L$

$V = \Pi \cdot R^2 \cdot L$

$V_{reactor} = 0{,}0143\ m^3$

$t_{residence} = V_{reactor} \cdot Flow_{fluidising\ gas}$

For a fluidising gas flow of 3,36 m^3/h:

$t_{residence} = 15{,}39\ s$

Figure 5.27.- LWS-V reactor dimensions

For each experiment only one parameter was changed and the others were kept constant in order to observe the influence of each variable on the pyrolysis reaction. The parameters modified were:

- Pyrolysis temperature
- Type of catalyst
- Amount of catalyst

Table 5.12.- Experiment conducted in LWS-V

Reactor	Catalyst	Ratio (weight)	Amount (wt %)	Temperature (ºC)	V (m^3/h) N_2	t residence (s)	PP feed (kg/h)	Sand diameter (mm)
LWS-V	WOC			400	3,36	15,39	1	3 - 5
	$TiCl_3$		1,0	400	3,3	15,6	1	3 - 5
	$TiCl_4$		1,0	400	1,75	29,42	1	1- 3
	$AlCl_3$		1,0	300	1,75	29,42	0,9	1- 3
				400	1,75	29,42	0,5	1- 3
	$TiCl_4$:$AlCl_3$	1:1	5,0	300	1,75	29,42	0,46	1- 3
				350	1,75	29,42	0,46	1- 3
				400	1,75	29,42	0,8	1- 3

5.2.3.1. Without catalyst

The experiment was run at a temperature of 400 °C. Once the reaction temperature was achieved, the feed screw was switched on. The reaction could only run during the first 30 minutes. Because after this time the amount of smelted PP interacts with the grains of sand. A conglomerate of PP and sand is the result. The new particles size is not homogeneous and therefore the temperature gradient can be enormous (temperature differences of 50 ºC). Under these conditions the fluidised bed reactor can not work properly.

When the reaction took place in the PR-I reactor, more than 40 wt% of polypropylene was still not pyrolysed after one hour of reaction at a pyrolysis temperature of 400 °C. The experiment run now in the LWS-V reactor confirmed that result: under such conditions the degradation reaction can not be conducted.

5.2.3.2. TiCl3

There was only one experiment with $TiCl_3$ as catalyst. Again the reaction temperature was 400 ºC. Because of the input of the catalyst, the LWS-V reactor had to be modified. A smaller silo with a capacity of 4 kg o PP (figure 5.28) was needed. Then the silo was put in a glove box to prepare the sample with the catalyst, which is reactive under oxygen conditions.

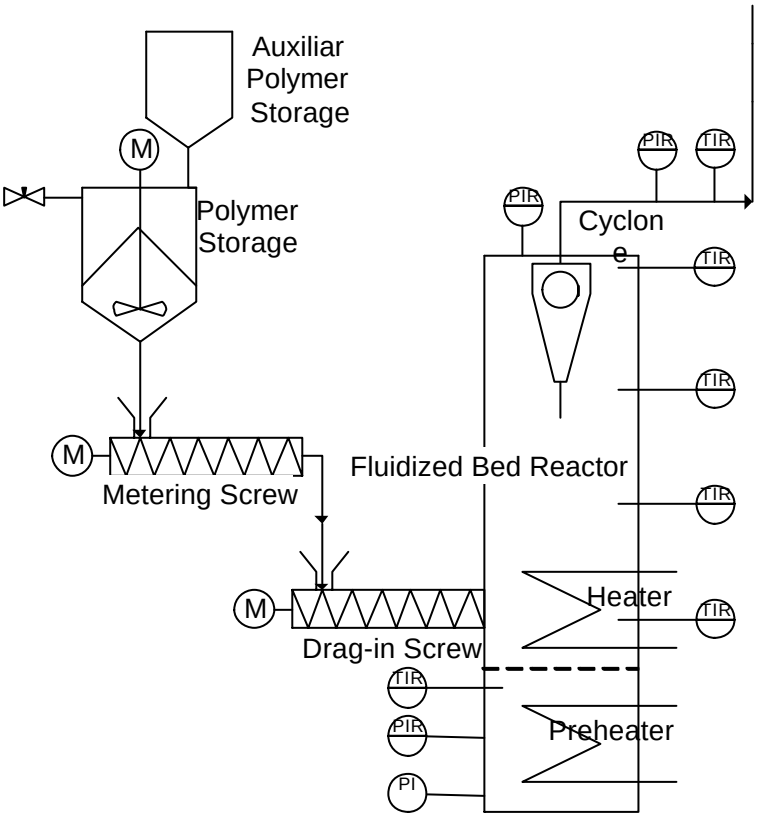


Figure 5.28.- LWS-V modification

Once the sample and the catalyst were prepared and properly mixed, the auxiliary silo was attached to the upper part of the already installed silo of the reactor and then opened.

Table 5.14, figure 5.30 and figure 5.31 show the products distribution and fractions obtained in the pyrolysis reaction.

5.2.3.3. $TiCl_4$

The experiment run with $TiCl_4$ as catalyst was conducted at a temperature of 400 ºC. As $TiCl_4$ is a liquid the fluidised bed installation had to be modified. A pump was installed to feed the catalyst into the silo where it was mixed with PP (figure 5.29).

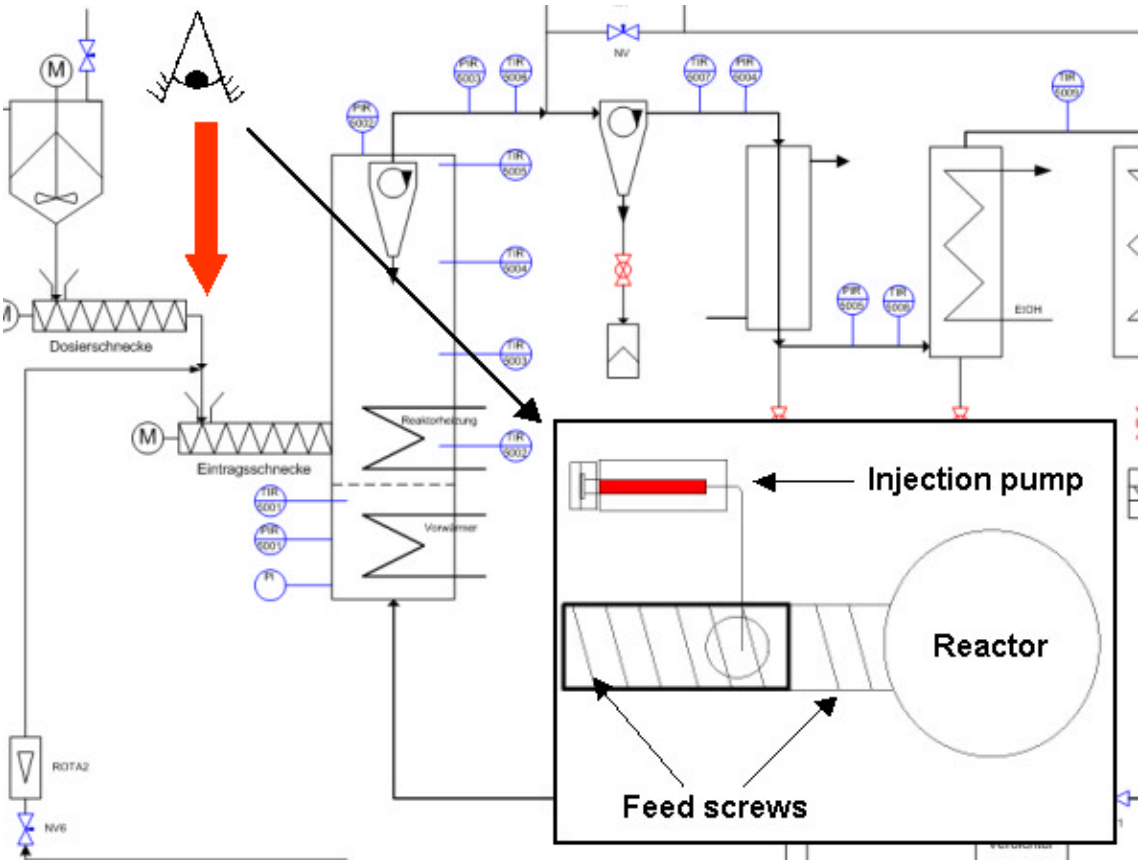


Figure 5.29.- Schema of LWS-V modification in the feed screws

The pump was an injection pump with which the liquid was injected accurately (6 mL/h of $TiCl_4$). The needle was situated between both feed screws with which the PP was fed. This installation made it possible to mix the catalyst and the PP just in the moment when the material was falling into the reactor.

Because of the experiences made in the precedent experiments (reaction without catalyst and reaction with $TiCl_3$) the fluidised sand was changed for a sand with identical physical properties but smaller diameter (01, - 0,3 mm). The smaller diameter made it possible to work with flows of 1,75 m^3/h (instead of with diameters of 3,3 m^3/h), As well the residence time increased from 15,6 s to 29,42 s. This caused that the pyrolysis reaction was more intense.

Table 5.14, figure 5.30 and figure 5.31 show the products distribution and fractions obtained in the pyrolysis reaction.

5.2.3.4. $AlCl_3$

2 experiments were conducted with $AlCl_3$ as catalyst, at 300 ºC as well as at 400 ºC. The pyrolysis temperature of 300 ºC was chosen because it was possible to run the pyrolysis reaction with $AlCl_3$ at this temperature in the batch reactor (chapter 5.2.2.4).

The installation of the LWS-5 reactor was the one shown in figure 4.28. The sample (PP and catalyst) was mixed in a glove box and the auxiliary silo was connected with the main silo. The sand diameter is displayed in table 5.12.

The reaction run at a temperature of 300 ºC finished but around 76 wt% PP was smelted and solidified in the reactor. At 400 ºC there were no problems to pyrolyse.

Table 5.14, figure 5.30 and figure 5.31 show the products distribution and fractions obtained in the pyrolysis reaction.

5.2.3.5. $TiCl_4 + AlCl_3$

Temperatures of 300 ºC, 350 ºC and 400 ºC were chosen to degrade PP in the fluidised bed reactor by using mixtures of $TiCl_4$ and $AlCl_3$ as catalyst. In these experiments the modifications described in previous chapters (5.2.3.2 and 5.2.3.3) had to be implemented together. The auxiliary silo was used to prepare the sample of PP and $AlCl_3$ in a glove box. For the input of $TiCl_4$ again the injection pump was installed. A mixture of PP and $AlCl_3$ was fed together into the reactor through the feed screws. $TiCl_4$ was injected as shown above and mixed with PP and $AlCl_3$.

Table 5.14, figure 5.30 and figure 5.31 show the products distribution and fractions obtained in the pyrolysis reaction.

5.2.3.6. Products

Table 5.13 shows the main products obtained. No products were obtained in the non-catalytic pyrolysis reaction at 400 ºC. By using a catalyst, it was possible to degrade the polymer at 400 ºC (from 87 wt% with $AlCl_3$ to 99,75 wt% with $TiCl_4$). It was even possible to decrease the temperature to 300 °C (with $AlCl_3$) and to 350 °C ($TiCl_4$:$AlCl_3$). But the degradation was not intense and only 24 wt% (1 wt% $AlCl_3$) and 26 wt% (5 wt% $TiCl_4$:$AlCl_3$) of the PP was pyrolysed at 300 ºC. After increasing the temperature to 350 ºC, and using the mixture of catalysts, 85 wt% of the material was pyolysed.

Table 5.13.- Experimental parameters

Catalyst	wt % cat.	T (ºC)	Total input material (g)	wt % pyrolysed PP	wt % gas	wt % light oil fraction	wt % heavy oil fraction	wt % not pyrolysed PP
WOC		**400**	2000,00	-	-	-	-	-
$TiCl_3$	**1,00**	**400**	3030,00	97,90	0,00	55,91	41,98	2,10
$TiCl_4$	**1,00**	**400**	3000,00	99,75	0,00	65,25	34,50	0,25
$AlCl_3$	**1,00**	**300**	2024,00	24,04	0,00	8,88	15,15	75,96
		400	1010,00	87,03	0,00	43,87	43,16	12,97
$TiCl_4$:$AlCl_3$ 1:1	**5,00**	**300**	910,00	26,48	0,00	19,77	6,72	73,52
		350	952,00	84,98	0,00	64,57	20,41	15,02
		400	1415,00	98,80	0,00	65,10	33,70	1,20

Figure 5.30 shows the product distribution in detail. Gas was not produced in any reaction: the gas counter did not indicate any production (amounts smaller than 0,5 %). Always (except at 300 ºC) the gasoline fraction (light oil fraction) was most produced. But it is important to remark that the light oil fraction and the heavy oil fraction production were equal when the reaction was run at 400 ºC with $AlCl_3$ as catalyst (≈ 43,5 wt%). When the reaction was run at lower temperatures the main amount in the total mass balance of the system was PP not pyrolysed (at 300 ºC over 73 wt%).

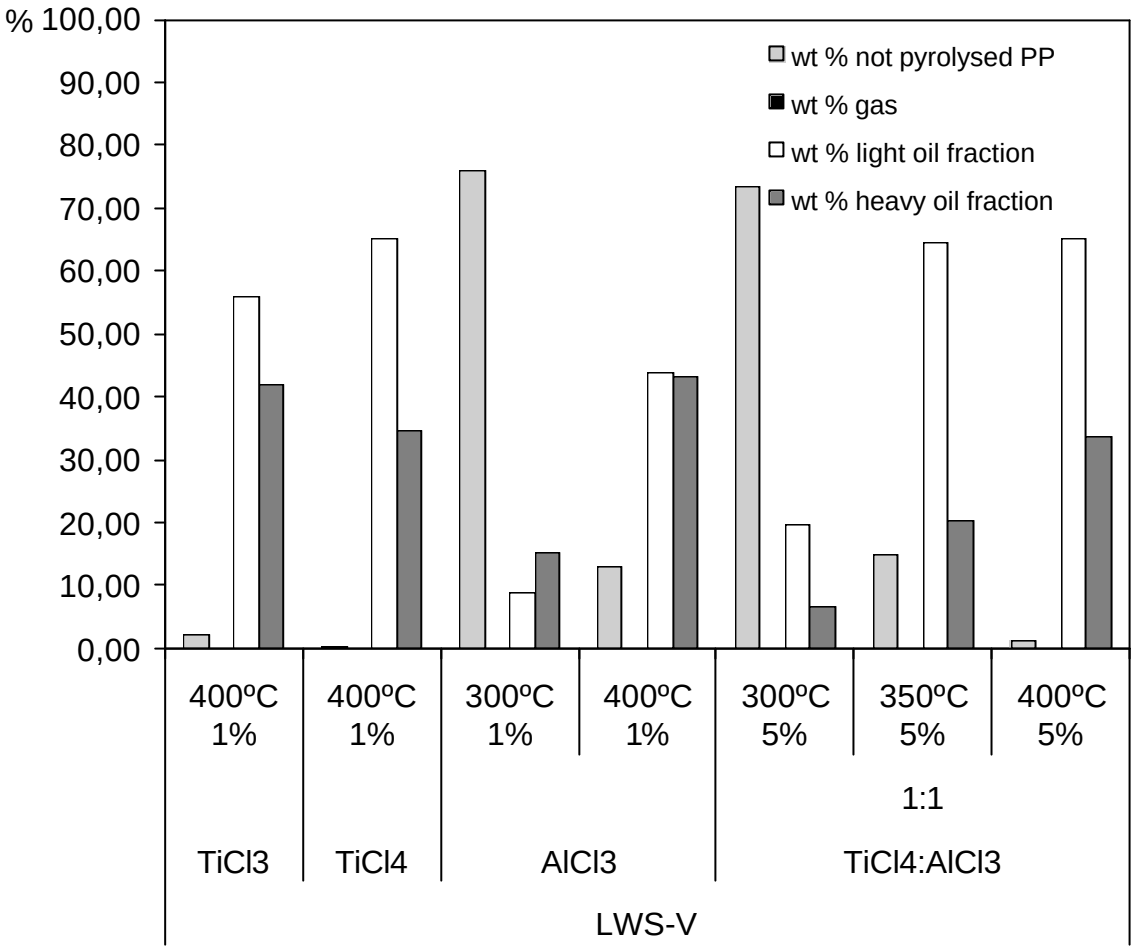


Figure 5.30.- Products distribution (wt %) of polypropylene's pyrolysis

Looking at the carbon number chains distribution of the results obtained in the batch reactor, it can be noticed that C9 fraction was the most important fraction when $TiCl_3$, $TiCl_4$, and $AlCl_3$ were used as catalysts. But when the pyrolysis reaction was carried out in the fluidised bed reactor, the C9 fraction was not predominant (lower than 12 wt%). The products distribution was more homogeneous , figure 5.31.

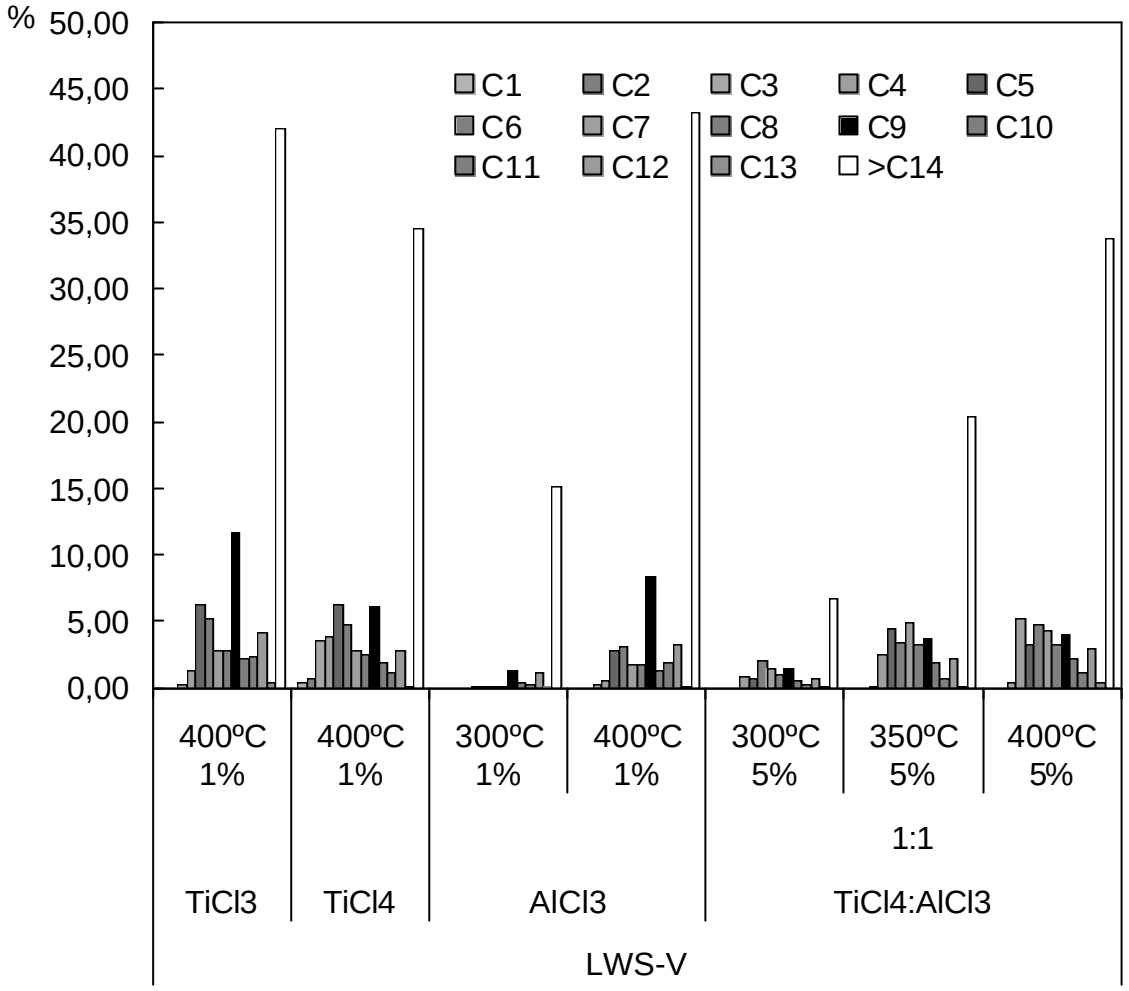


Figure 5.31.- Product fractions of polypropylene's pyrolysis

The gas chromatographers spectrums (figure 5.32) indicate that using a mixture of catalysts the peaks distribution of the fractions is more homogeneous. The peaks number is higher than at the same temperature using $TiCl_3$.

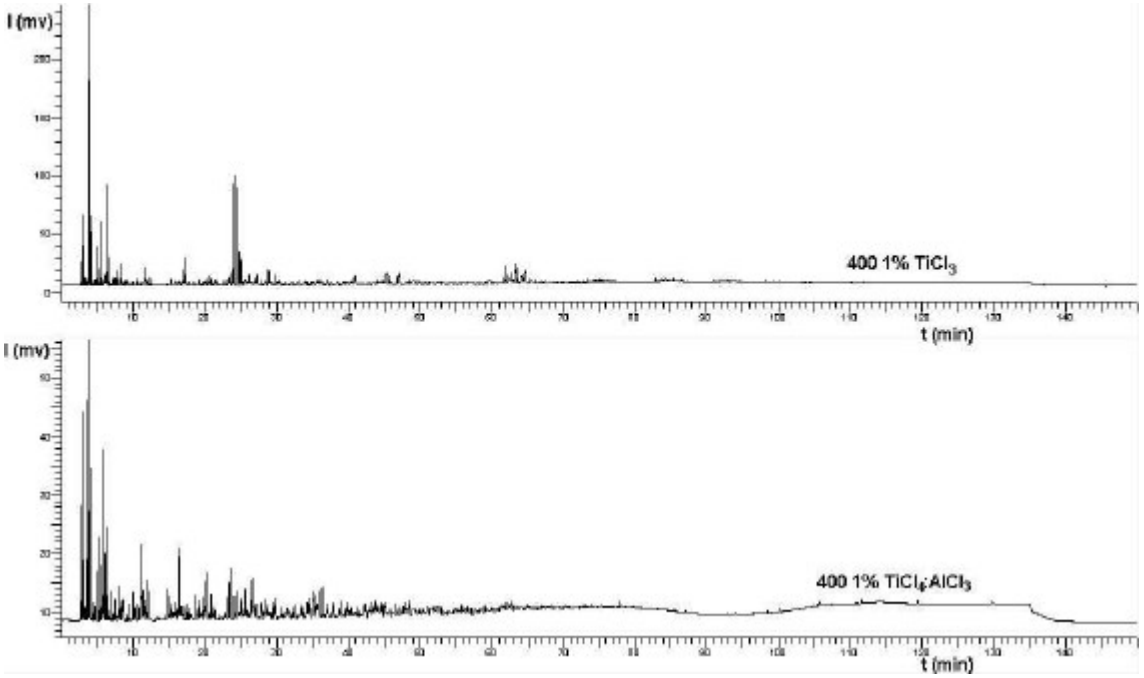


Figure 5.32.- Light oil chromatograms of LWS-V experiments

Table 5.14.- Main single product components of the pyrolysis of PP using LWS-V

	LWS-V						
	$TiCl_3$	**$TiCl_4$**	**$AlCl_3$**		**$TiCl_4$:$AlCl_3$ 1:1**		
	400ºC 1%	**400ºC 1%**	**300ºC 1%**	**400ºC 1%**	**300ºC 5%**	**350ºC 5%**	**400ºC 5%**
Component (gas + light oil)							
Hydrogene	1,68	1,09	0,00	0,00	0,00	0,00	0,00
Methane	0,00	0,45	0,00	0,00	0,00	0,00	0,00
Ethane	0,00	0,55	0,00	0,00	0,00	0,00	0,00
Ethene	0,00	0,21	0,00	0,00	0,00	0,00	0,00
Propane	0,00	0,33	0,00	0,00	0,00	0,00	0,00
Propene	0,28	3,19	0,00	0,32	0,00	0,11	0,36
1-Butene	0,00	0,13	0,00	0,00	0,00	0,00	0,00
1,3-Butadiene	0,00	0,55	0,00	0,00	0,00	0,00	0,00
2-Methyl-propene	0,99	1,14	0,00	0,08	0,14	0,60	1,46
2-Butene	0,28	2,00	0,00	0,41	0,78	1,92	3,73
2-methyl-1-pentene	1,97	1,19	0,05	0,99	1,11	0,66	1,25
2,3-Dimethyl-2-butene	1,86	2,29	0,02	1,44	0,19	1,29	1,60
2-Methyl-2-hexene	1,12	1,03	0,01	0,57	0,77	3,04	1,99
2,4-Dimethyl-1-heptene	8,30	1,82	1,22	4,61	0,37	0,94	1,49
2,3,7-Trimethyl-2-octene	0,88	0,20	0,06	0,82	0,05	0,11	0,46
3-Methyl-3-undecene	0,42	0,62	0,04	0,22	0,20	0,56	0,56
7-Methyl-1-undecene	0,39	0,34	0,22	0,56	0,07	0,12	0,46
wt % heavy oil fraction	41,98	31,47	15,15	43,16	6,72	20,41	33,70

5.3. Energy and economical balance

The study of the energy balance is a must after the mass balance studied to calculate the economical cost of the process. The balance was carried out using the parameters of the LWS-V pilot plat .

Extra data from Dr. Donner's thesis [98] were used to calculate LWS-V energy requirement at high temperatures up to 700 ºC (table 5.15). All data are collected from an energy meter installed in the system.

Table 5.15.- LWS-V energy consumption

Experiment	Temperature (ºC)	Reactor consumption (kWh)	Compressor consumption (kWh)	Time (h)
Topas	700	5,70	3,40	1,25
Topas	650	5,80	3,00	1,40
WOC	400	1,80	1,60	1,00
$TiCl_3$	400	3,80	3,53	2,25
$TiCl_4$	400	8,80	3,40	3,58
$AlCl_3$	300	4,50	-	2,75
AlCl3	400	5,60	3,70	3,50
$TiCl_4$:$AlCl_3$	300	3,95	3,60	3,50
$TiCl_4$:$AlCl_3$	350	3,80	2,80	2,75
$TiCl_4$:$AlCl_3$	400	6,65	3,40	2,25

Figure 5.33 shows the energy cost in one hour reaction and the average of them at each temperature.

in previous chapters, it was described the possibility to decrease the pyrolysis temperature 100 ºC up to 300 ºC depending of the reaction conditions as well the catalyst used. There are two parameters to take into consideration to study the economical balance:

- The energy saved when the reactor temperature is decreased.
- The catalyst amount used.

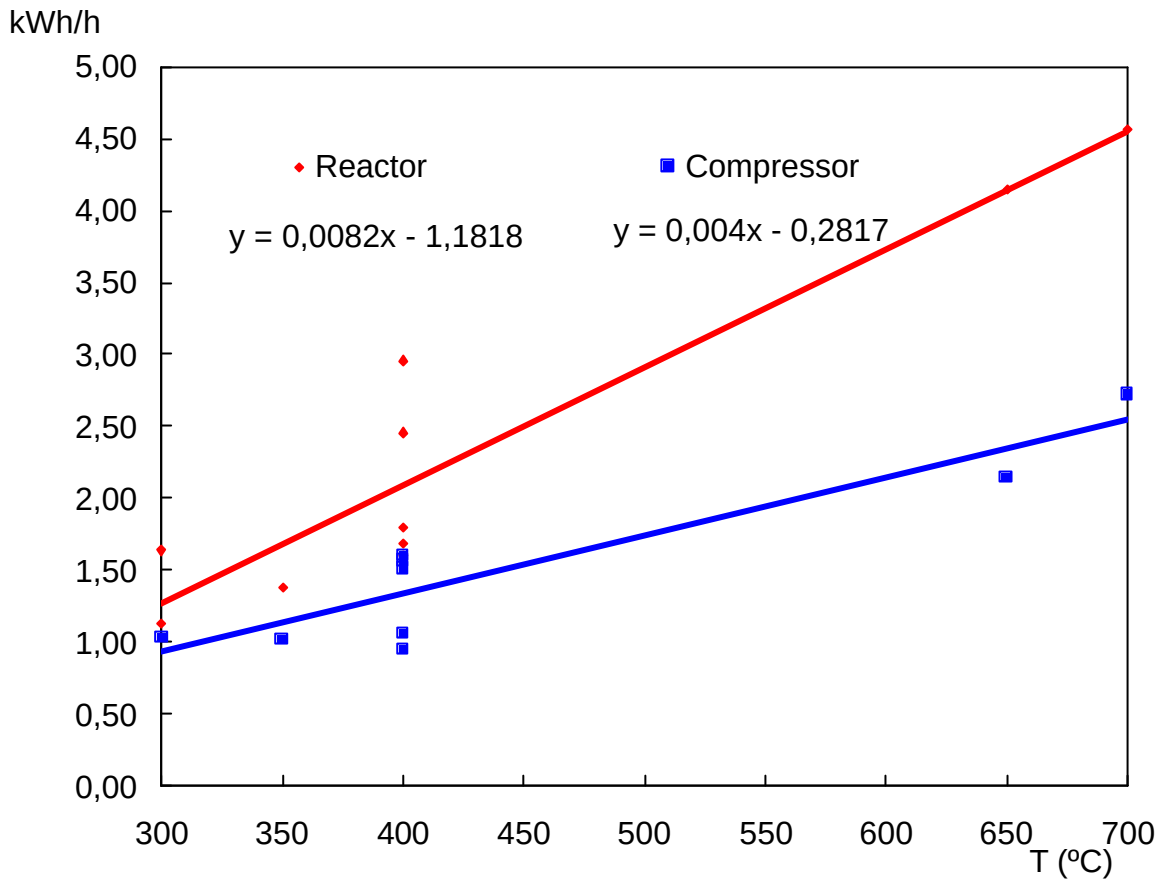


Figure 5.33.- Reactor and compressor energy requirements per hour

Table 5.16 shows the energy requirements of the reactor per hour in an stationary state.

Table 5.16.- Reactor's energy consumption average

Reactor consumption(kWh)	Temperature (ºC)
1,28	300
1,69	350
2,10	400
2,92	500
3,74	600
4,15	650
4,56	700

Considering the actual (September 2006) price of the electrical energy supplied (0,17 €/kWh) (table A.6), the energy saved, and the capital saved in function of the temperature decreased per hour is (table 5.17):

Table 5.17.- Energy and capital saved per hour and year supposing 24 h/day operation

DT (ºC)	Energy saved (kWh)/h	Capital saved (€)/h	Capital saved (€)/year
(500 ºC – 400 ºC) 100 ºC	0,82	0,14	1221,14
(600 ºC – 400 ºC) 200 ºC	1,64	0,26	2442,29
(600 ºC – 300 ºC) 300 ºC	2,46	0,42	3663,43

The amount of catalyst used to decrease the temperature and the cost of it is the other factor to be considered. Considering feed of 1 kg/h of PP and 1% of catalyst used, the amount of catalyst used are 10 g/h. Supposing that the plant operates 24 h/day, the total amount of catalyst needed are 87,6 kg/year.

The MERCK chemical prices given for these amounts are:

Table 5.18.- Merck chemical prices

Catalyst	Amount/year	Price	Capital (€/year)
$TiCl_3$	87,60 kg	24,60 €/kg	2154,10
$TiCl_4$	51,00 L	20,00 €/L	1020,00
$AlCl_3$	87,60 kg	11,14 €/kg	976,00

Table 5.19 indicates the percentage of capital saved per year depending the reaction conditions and catalyst used.

Table 5.19.- Percentage of capital saved

	DT (ºC)		
Catalyst	(500 ºC – 400 ºC) 100 ºC	(600 ºC – 400 ºC) 200ºC	(600 ºC – 300 ºC) 300 ºC
$TiCl_3$	-16,76 %	5,18 %	27,11 %
$TiCl_4$	3,61 %	25,55 %	47,48 %
$AlCl_3$	4,40 %	26,34 %	48,27 %

Concluding, the degradation of pyrolysis in a fluidised bed reactor LWS-V decreasing the temperature more than 200 ºC results cheaper than the conditions without catalyst.

6. CONCLUSIONS

By comparing the results obtained in the thermal cracking reaction with those obtained in the catalyric cracking reaction, the conclusion can be drawn that the use of Ziegler-Natta catalysts makes the pyrolysis reaction effectively run at lower temperatures. Results obtained in experiments carried out with catalysts at a pyrolysis temperature of 400 °C are similar to the results of the non-catalytic reaction which was run at 500 °C. This means that the decrease of the temperature is possible.

The catalytic systems even permit to conduct reactions at temperatures at witch a non catalytic pyrolysis reaction is not possible anymore. For example, by using $AlCl_3$, PP was pyrolysed at a temperature of 300 °C. Under non catalytic conditions, PP was not pyrolysed at this temperature.

With regard to the product distribution, the experiments showed that the catalytical degradation produced high yields of gasoline as well as of other distillates and low gas fractions . But it has to be mentioned as well that too high amounts of the catalyst also had negative effects on the product selectivity caused by secondary reactions.

By running catalytical reactions at a temperature over 500 °C, the catalyst was decomposed. The tar amount increased independently from the catalysts used in all reactions carried out at this temperature. Furthermore, the C9 fraction obtained in the experiments run with catalyst at 500 °C was lower than the yield of the reaction run at 400 °C under same conditions.

Interesting in an industrial point of view is that the energy consumption and the economical balance (process costs) can be reduced if Ziegler-Natta- catalysts are used. For example, the heating costs of LWS-V were reduced by half by using the catalysts. It has to be mentioned that the conditions and efficiency are

not optimal in this reactor, small scale and kind of heating system (electrical heating system vs propane or gas heating systems).

The use of chlorinated compounds could present environmental and corrosion problems that shall be studied in future steps of the researching work, but conducting wickbold analysis to determinate chlorinated compounds gave results under 50 ppm after a washing treatment of the sample to be analysed.

Concluding, the researched technology could be implemented very well in the petrochemical industry. A pyrolysis industrial plant could be placed close to a refinery treating the different fractions produced. A post treatment in refinery of the light oil fraction could be used a gasoline for automotives. A comparison of the gasoline fraction with the light oil fraction obtained in a pyrolysis reaction shows that these fractions are similar (figure 6.1). The other fractions could be reformed in refinery process.

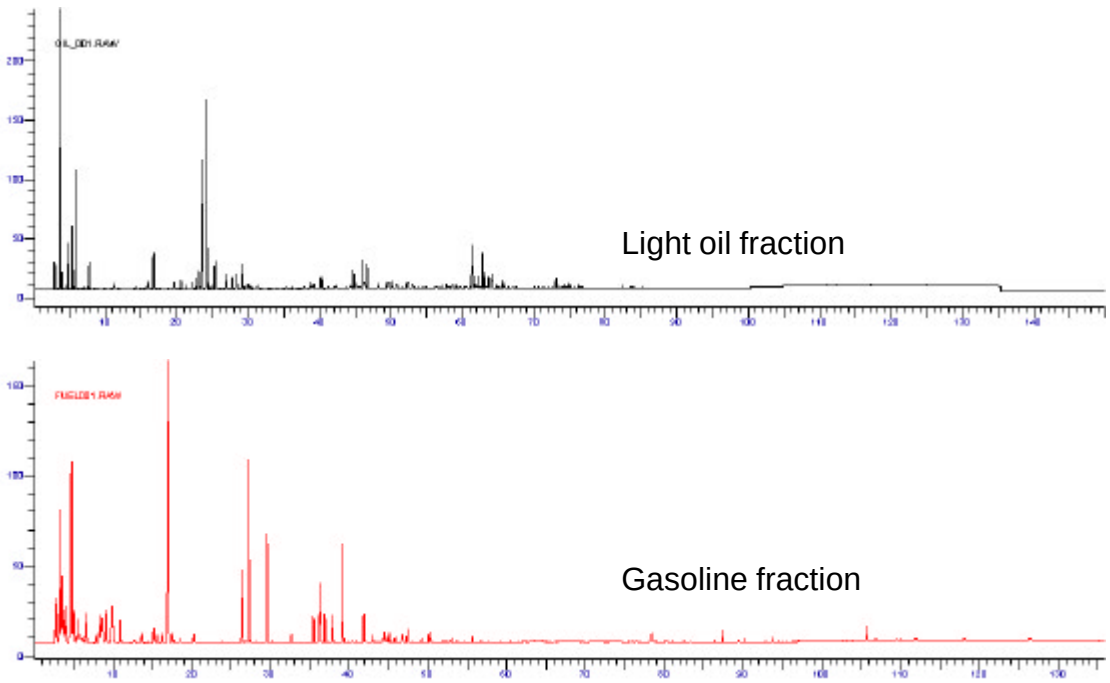


Figure 6.1.- Gas chromatograph comparison between a pyrolysis light oil fraction and a commercial gasoline sample.

7. EXPERIMENTAL PART

7.1. Analysis

7.1.1. Differential-Scanning-Calorimetry (DSC)

Melting temperatures, Tm, crystallization temperatures (Tc) and glass-transition temperatures (Tg) were determined by differential scanning microscopy (DSC) with a DSC 821e (Mettler- Toledo) calibrated with indium (Tm = 156.6 °C), cyclopentane (Tm = -93.9°C) and water (Tm = 0.0°C). Generally, samples of 5-6 mg were used for DSC analysis. Data for the Tm was taken from the heating curve of the second heat at a heating rate of 20 °C/min in the range of –100 to 200 °C. Crystallization temperatures, Tc, were determined by DSC from the cooling curve (cooling rate 10 °C/min) after complete melting at 200 °C for 5 min. Isothermal crystallization was performed by quenching the sample to the desired temperature (cooling rate 40 °C/min) after complete melting at 200 °C for 5 min.

7.1.2. ^{13}C-NMR-Spectroscopy

All ^{13}C-NMR-spectra were recorded ^{1}H-decoupled on a Bruker Ultrashield 400-Spectrometer at 100°C. The parameters of the measurements are listed in table 7.1.

Table 7.1.- Parameters of NMR-measurements

Decoupling	BB, Waltz 16 pulse program
Frequency	100.62 MHz
Number of Scans	1024
Pulse Angle	60°
Relaxation Time	5 s
Sweep-Width:	25126 Hz

Samples were prepared from approximately 200 mg polymer, 4 g trichlorobenzene and 0.5 g tetrachloroethane-d2 (TCE-d2) in a 10 mm NMR-sample-tube. The chemical shift was measured relative to the TCE-d2-signal at 74.24 ppm, and spectra were evaluated using the program SpecView (ACD).

7.1.3. Gel-Permeation-Chromatography

Gel permeation chromatography was carried out with a Waters GPC 2000 Alliance system equipped with a refractive index detector, viscosimetric detector and a set of three columns, Styragel type. The particle size for each column was 10 µm, and the pore sizes were 103 Å (HT3), 104 Å (HT4), and 106 Å (HT6). 1,2,4-Trichlorobenzene was used as solvent. The analyse were performed at 140 °C and 1.0 mL/min. The columns were calibrated with narrow molar mass distribution polystyrene standards. The sample concentration was 1 mg/mL and the injection volume 215 µL. 2,6-Di-*tert*butyl-4-methylphenol was used as thermostabilizer. The samples were filtered using a GPC vial equipped with a filter before the measurements to remove the filler. The Mark-Houwink constants were calculated automatically by the Millenium software supplied by Waters from the values measured with the visco- and refractive index-detectors.

7.1.4. Pyrolysis–gas chromatograph–mass spectrometer

Pyro-GC/MS measurements were carried out in a Shimadzu PYR-4A Pyrolyzer, GC, Shimadzu GC-17A and MS, Shimadzu QP5000, J&W Scientific DB-5MS. The calibration of the device was carried out with a PFTBA-Standard. The samples weight was around 100 µg prepared in a platinum bucket. The bucket was situated over the pyrolyser and once the system was properly closed the period of time to evacuate the air form the system was 10 min. After this period of time the device was ready to analyse the sample.

The device parameters are described in table 7.2.

Table 7.2.- Analysis parameters of the Py-GC/MS

GC/MS	Shimadzu QP5000
Pyrolyser	Shimadzu Pyr-4A
Ionizer	Electron collision (EI)
Ionization energy	70 eV
Carrier gas	Helium 5.0, pressure 30 kPa
Mass range	10 – 500 m/z
Scan speed	500 amu·s-1
Detector tension	1 kV
Scan interval	1 s
Separation column	J&W Scientific DB-5MS (L = 60 m, ID = 0,32 mm, Film thickness = 1 µm)
Column flow	1,1 mL·min-1
Split	1:80
Temperature program	35 °C (8,5 min) $\rightarrow$ 2 °C·min^{-1} $\rightarrow$ 50 °C (0 min) $\rightarrow$ 10 °C·min^{-1} $\rightarrow$ 290 °C (20 min) = Σ 60 min
Pyrolysis temperature	300 – 800 °C
Sample weight	100 µg
Interface temperature	300 °C

The software used to the control the system was CLASS5K V.2.23 and the software used to interpret and treat the results was GCMSsolution V.2.20. Both developed by Shimadzu.

7.1.5. Gas chromatograph

7.1.5.1. Analysis of gases

Gas chromatography was carried out with a flame ionization detector (GC–FID, Chrompack CP 9002, Chrompack CP-Al_2O_3/KCl-Plot) for the hydrocarbons and by gas chromatography with a thermal conductivity detector (GC–TCD, Chrompack CP 9001, Chrompack Carboplot® P7) for the permanent gases (N_2, H_2, CO,CO_2). Both measurements were correlated via methane and the response factors of the hydrocarbons were calculated. The response factors of the permanent gases were obtained from Schlesselmann [99] method. Table 7.5 shows the response factors of the gases where F_i is the peak surface of he components.

The analyse parameters and methods are described in the tables 7.3 and 7.4.

Table 7.3.- Method of the gas chromatograph to analyse the permanent gases

Gas chromatograph	Chrompack CP 9001
Separation column	Chrompack CarboPLOT P7 (25 m, 0,53 mm, 25 µm)
Reference column	Chrompack PoraPLOT Q (10 m, 0,32 mm, 10 µm)
Carrier gas	Argon, Pressure $_{separation\ column}$: 36kPa,
	Pressure $_{reference\ column}$: 44 kPa
Column flow	3,7 mL·min^{-1}
Sample	1 mL sample loop, Split 1:2
Detector	WLD, 150 °C
Temperature program	35 °C (1,5 min) → 15 °C·min^{-1} →115 °C (13 min)
Data logging	Interface PE Nelson 900, Turbochrom Navigator 4.1

Table 7.4.- Method of the gas chromatograph to analyse the hydrocarbon gases

Gas chromatograph	Chrompack CP 9002
Separation column	Chrompack CP-Al2O3/KCl (50 m, 0,32 mm, 5 µm)
Carrier gas	Hydrogen 5.0, Pressure $_{separation\ column}$: 100 kPa
Column flow	3,5 mL·min^{-1}
Sample	1 µL sample loop, Split 1:30
Injector	250 ºC
Detector	FID, 250 °C
Temperature program	100 °C (5 min) → 10 °C·min^{-1} → 200 °C (30 min)
Data logging	Interface PE Nelson 900, Turbochrom Navigator 4.1

Table 7.5.- Response factors for the TCD detector

Permanent gas	Response factor R_i
Nitrogene	1
Hydrogene	$6 \cdot 10^{-3} + 5 \cdot 10^{-6} F_{H2}$
Carbon monoxide	$1,49 – 8,1 \cdot 10^{-3} F_{CO}$
Carbon dioxide	$1,7118 – 3,9 \cdot 10^{-3} F_{CO2}$
Methane	$0,2028 – 0,2 \cdot 10^{-3} F_{CH4}$

The method described by Jorgensen et al. [100] was used to calculate the response factors and to calculate the mass amount of each component in the

sample in FID devices (table 7.5). The FID response of hydrocarbons is generally proportional to the mass of carbon present in the sample, but the degree of signal reduction due to partially oxidized carbon atoms in heteroatomic compounds varies markedly with heteroatom and bond types. Compounds that contain, for example, oxygen, nitrogen, or halogens give varied responses but can be quantified by the FID if corrections are made for the usual loss of sensitivity caused by the presence of these atoms in various functional groups. To determinate the response factor is used the following mathematical prediction.

$$R_i = \frac{ECN_{Np} \cdot MW_i}{ECN_i \cdot NW_{Np}}$$

in which:

R_i = Response factor of component i

ECN_{Np} = Effective Carbon Number of naphthalene

ECN_i = Effective Carbon Number of component I

MW_{Np} = Molar mass of naphthalene

MW_i = Molar mass of component i

For the non-identified components the response factor used is an average of the response factors used and the amount of them in the sample.

$$m_i = \frac{R_i \cdot F_i}{\sum_i R_i \cdot F_i} \cdot 100$$

in which:

m_i = Portion of the substance i [m%]

R_i = Response factor of the substance i

F_i = Peak surface of the substance i

The qualitative analysis of the gas components was carried out with a mass spectrometer VG 70 SE from the company FISIONS INSTRUMENTS. Table 7.6 shows the parameters used for the analysis.

Table 7.6.- Gas chromatograph method for the qualitative analysis

Gas chromatograph	Hewlett Packard 5890
Separation column	Machery & Nagel SE52 (50 m, 0,25 mm, 0,5 µm)
Carrier gas	Helium 5.0, $Pressure_{separationcolumn}$: 85 kPa
Column flow	3,0 $mL \cdot min^{-1}$
Sample	0,1 µL, Split 1:50
Injector	270 ºC
Temperature program	30 °C (10 min) → 2 $°C \cdot min^{-1}$ → 120 °C (0 min) → 3 ºC min^{-1} → 270 ºC (30 min)
Mass spectrometer	Fissions Instrument VG 70 SE
Ionizer	Electron collision (EI)
Ionization energy	70 eV
Beam potential	8 kV
Scan speed	1 amu · s^{-1}
Mass range	30 – 500 m/z
Data logging	Opus V3.21 under Open VMS (Alpha station 255)

The interpretation of the analysis was carried out with the software Masslib V.8.7.

7.1.5.2. Analysis of oil fraction

The oil fraction was characterized by GC–FID (HP 5890, Macherey & Nagel SE 52) and GC–MS (GC: HP 5890, MS: Fisons Instruments VG 70 SE, Macherey & Nagel SE 52).

Table 7.7.- Method of the gas chromatograph to analyse the oil fraction

Gas chromatograph	Hewlett Packard 5890
Separation column	Macherey and Nagel, SE-52 (50 m, 0,25 mm, 0,5 µm)
Carrier gas	Helium 5.0, $Pressure_{separationcolumn}$: 130 kPa
Column flow	3,0 $mL \cdot min^{-1}$
Sample	1 µL, Split 1:30
Injector	290 ºC
Detector	FID, 300 °C
Temperature program	30 ºC (10 min)?→ 2 ºC/min^{-1} →120 ºC (0 min)?→ 3 ºC/min^{-1}?→ 300 ºC (30 min)
Data logging	Interface PE Nelson 900, Turbochrom Navigator 4.1

The qualitative analysis of the oil components was carried out with a mass spectrometer VG 70 SE from the company FISIONS INSTRUMENTS. Table 7.8 shows the parameters used for the analysis.

Table 7.8.- Gas chromatograph method for the qualitative analysis

Gas chromatograph	Hewlett Packard 5890
Separation column	Chrompack CP-Al_2O_3/KCl (50 m, 0,32 mm, 5 µm)
Carrier gas	Helium 5.0, $Pressure_{separationcolumn}$: 80 kPa
Column flow	3,0 $mL \cdot min^{-1}$
Sample	2 mL gas closed syringe, Split 1:50
Injector	270 ºC
Temperature program	100 °C (5 min) → 10 °C·min^{-1} → 200 °C (30 min)
Mass spectrometer	Fissions Instrument VG 70 SE
Ionizer	Electron collision (EI)
Ionization energy	70 eV
Beam potential	8 kV
Scan speed	1 amu · s^{-1}
Mass range	30 – 500 m/z
Data logging	Opus V3.21 under Open VMS (Alpha station 255)

7.1.5.3. Analysis of wax fraction

In the same way the wax fraction was analyse in the FID detector. In this case it was used a polyethylene standard with a chain length of $C_{10} – C_{100}$ (Poliwax®) to correlate the results.

Table 7.9.- Method of the gas chromatograph to analyse the wax fraction

Gas chromatograph	Hewlett Packard 5890 SII
Separation column	Varian WCOT Ulti-Metal CP SimDist CB (10 m, 0,53 mm, 0,17 µm)
Precolumn	Varian Retention Gap
Carrier gas	Helium 5.0, Pressure $_{separation\ column}$: 350 kPa
Column flow	2,5 mL·min^{-1}
Sample	0,5 µL
Injector	300 ºC(On-Column)
Detector	FID, 430 °C
Temperature program	30 °C (5 min) → 10 °C·min^{-1} → 430 °C (15 min)
Data logging	Interface PE Nelson 900, Turbochrom Navigator 4.1

7.1.6. Elemental analysis

The elemental analysis was carried out on a Carlo Erba CHN analyzer EA 1106 CHNS-O in the research group of Professor Dr. J.A.C. Broekaert, elemental analysis service of the inorganic chemistry institute, University of Hamburg. It was possible to determine the percentage by mass of the hydrogen, carbon and nitrogen elements.

7.1.7. Karl–Fischer analysis (water content)

The water content was determined by titrating following the Karl–Fischer method (Methrom E 547, ISO 8534). This method calculates the oxidation of Sulphur dioxide with iod under stoichiometric conditions with water.

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

The titration was carried out with a the Karl-Fischer reagent form Merck.

7.1.8. Determination of Ash content

The determination of the ash content was carried out under the norm DIN 51719 for the inorganic materials as well the fluidised bed agents. 40 to 120 g of material are deposited in a porcelain crucible with a precision of 0,001g. It is heated until 815 ºC ± 15 ºC were the material is calcined. Once the temperature decreases it is measured again. The weight difference is the ash content of the sample.

7.1.9. Determination of chlorine content

Chlorine ion content of the oil fractions was determined by the Wickbold method. The Wickbold method (DIN 51408) consists in combusting a sample of the sample in a hydrogen-oxygen flame in a Wickbold apparatus and absorbing the hydrogen chloride produced in the combustion process in double-distilled or deionised water. The absorbed hydrogen chloride is then determined by a potentiometer titration with a solution 0,002 M of silver nitrate determinate in a sulphuric acid medium. The precision of the result is around 0,1 ppm (0,1 mg/kg).

7.2. Waste disposal

The waste disposal, as well the contact with dangerous chemicals takes place following the regulation conformity of the chemicals law (ChemG) [101] and the ordinance on hazardous substances (GefStoffV) [102].

The solvents are separated and disposed in security-containers for halogen-free and halogen compounds. Then the are transported to the waste disposal section. The same for organic and watery phases properly separated before. The contaminated material is collected as well and disposed in the appropriate place. Pyrophorus compounds are first diluted in toluene under argon atmosphere, afterwards 2-propanol is used in the diluted solution finishing with ethanol and chlorhydric acid solution to decompose it.

7.3. Safety instructions

The safety instructions of the chemical products are in table 7.10 [103]:

Table 7.10.- Safety instructions

chemical substance	symbol	risks	safety
2-Propanol	F, Xi	11-36-67	7-16-24-26
Acetone	F	11-36-66-67	9-16-26
Aluminium (III) chloride	Xi	36/38	S 7/8-28.1-45
Argon	Xi	-	-
Ethanol	F	11	7-16
Hydrochloric acid (36 wt.-%)	F, Xi	34-37	26-36/37/39-45
Hydrogen	F^+	12	9-16-33
Methane	F	12	9-16-33
Titanium (III) chloride	C	34-37	26-36/37/39-45
Titanium (IV) chloride	C	14-34	7/8-26-36/37/39-45
Toluene	F, Xn	11-20	16-25-29-33

8. NOMENCLATURE

$AlCl_3$:	Aluminium (III) chloride
ASR:	Automotive shredder residues
FID:	Flame ion detector
GC:	Gas chromatograph
GPC:	Gel-Permeation-Chromatography
HD-PE:	High density polyethylene
LD-PE:	Low density polyethylene
LWS-V:	Laborwirbelschichtanlage V
MS:	Mass spectrometer
MSW:	Municipal solid waste
PAN:	Polyacrylonitrile
PB:	Polybutadiene
PE:	Polyethylene
PES:	Polyethylstyrene
PET:	Polyethylene terephthalate
PIB:	Polyisobutene
PMAN:	Polymethacrylonitrile
PMMA:	Polymethylmethacrylate
PP:	Polypropylene
PR-I:	Pyrolysis reactor I
PS:	Polystyrene
PTFE:	Polytetrafluoroethylene
PU:	Polyurethane
PVC:	Polyvinyl chloride
PVF:	Polyvinylfluoride
Pyro-GC/MS:	Pyrolysis–gas chromatograph–mass spectrometer
RCP:	Recycled Clean Product
$TiCl_3$:	Titanium (III) chloride
$TiCl_4$:	Titanium (IV) chloride
TWS:	Technikumwirbelschichtanlage

9. LITERATURE

1. APME, *Good Practices Guide on waste Plastics Recycling. A guide by and for local and regional authorities.* www.apme.org, 2004.
2. Brandrup, J.B., M.; Menges, G.; Michaeli, W. (Eds), *Recycling and recovery of plastics.* Hanser Publishers, Munich, 1996.
3. Vandenberg, E.J.S., J.C. (eds.), *Catalysis in polymer synthesis.* ACS Symp. Ser., 1992. **496**: p. 1.
4. Zucchini, U., Makromol. Chem. Makromol. Symp., 1993. **66**: p. 25-42.
5. Soga, K., Makromol. Chem. Makromol. Symp., 1993. **66**: p. 43-54.
6. Ystenes, M., Makromol. Chem. Makromol. Symp., 1993. **66**: p. 71-82.
7. Guerra, G.e.a., Makromol. Chem. Makromol. Symp., 1993. **69**: p. 237-249.
8. Simonazzi, T.G., U., Gazz. Chim. Ital., 1994. **124**: p. 533-541.
9. Wilke, G., Angew. Chem. Int. Ed., 1988. **27**: p. 185.
10. Keim, W., Angew. Chem., 1990. **102**: p. 251-260.
11. Ziegler, K., *Results and development of a discovery.* Angew. Chem., 1964. **76 (13)**: p. 545-553.
12. Ziegler, K., *Alumino-organic syntheses in the field of olefinic hydrocarbons.* Angew. Chem., 1952. **64**: p. 323-329.
13. Ziegler, K.H., E.; Breil, H.; Martin, H., *The Mühlheim low-pressure polyethylene process.* Angew. Chem., 1955. **67**: p. 541-547.
14. Ziegler, K.B., H.; Holzkamp, E.; Martin, H., *Verfahren zur Herstellung von hochmolekularen polyäthylenen.* Germany DE 973626, 1953.
15. Böhm, L.L., *The ethylene polymerization with ziegler catalysts: Fifty years after the discovery.* Angew. Chem. Int. Ed., 2003. **42 (41)**: p. 5010-5030.
16. Natta, G., *Stereospecific catalysis of isotactic polymers.* Angew. Chem., 1956. **68**: p. 393-403.
17. Natta, G., *From stereospecific polymerization to the asymmetric autocatalytic synthesis of macromolecules.* Angew. Chem., 1964. **76 (13)**: p. 553-566.
18. Natta, G.C., G., *Properties of ethylene-propylene copolymers and of terpolymers containingunsaturation* J. Polym. Sci., 1962. **61 (171)**: p. 83-95.
19. Sinclair, K.B., Wilson, R.B., Chem. Ind. (London), 1994: p. 857-862.
20. Sinn, H.K., W., Adv. Organomet. Chem., 1980. **18**: p. 99.
21. Kaminsky, W., Catal. Today, 1994. **20**: p. 257-271.
22. Kaminsky, W., Angew. Makromol. Chem., 1994. **223**: p. 101-120.
23. Möhring, P.C.C., N.J., J. Organometal. Chem., 1994. **479**: p. 1-29.
24. Kaminsky, W.S., H., *Pyrolitic techniques*. Recycling and recovery of plastics, ed. J. Brandrup. 1996, Munich: Hanser Publishers. 434-444.
25. Brophy, J.H.H., S., *Low temperature pyrolysis for feedstock preparation*. Recycling and recovery of plastics, ed. J. Brandrup. 1996, Munich: Hanser Publishers. 422-433.
26. Scheirs, J. Polymer recycling science, technology and applications. 1998, New York: J. Wiley & Sons.

27. Kaminsky, C.M.S.C.E.H.K.W., *Chemisches Recycling von Kunststoffen mittels Wirbelschichtpyrolyse*. DGMK Berichte; Tagungsbericht 9603, ed. DGMK. 1996: DGMK. 337-344.
28. Kaminsky, W., *Pyrolyse von Kunststoffen in der Wirbelschicht*. Erfassung und Verwertung von Kunststoff, ed. H. Sutter. 1993, Berlin: EF-Verlag. 187-201.
29. Sinn, H., *Recycling of plastics.* Chem. Ing. Techn., 1974. **46**: p. 579-589.
30. *Fluidized-bed reactors*. 2 ed. Chemical engineering Kinetics. 1970, New York: McGraw-Hill. 549-557.
31. *The Petroleum Handbook*. 6 ed, ed. R.D.S.G.o. Companies. 1983: Elsevier. 233,234,279-284.
32. *Wirbelschichtreaktoren*. Verfahrenstechnische Berechnungsmethoden. 5.: Chemische Reaktoren, ed. VCH. Vol. 5. 1987, Weinheim: VCH. 231-244.
33. *1988 Refining Handbook.* Hydrocarbon Processing, 1988(9): p. 61-91.
34. *Petrochemical Handbook ´89.* Hydrocarbon Processing, 1989(11): p. 85-115.
35. *Refining Handbook '92.* Hydrocarbon Processing, 1992(11): p. 137-211.
36. Kaminsky, W.M., J.; Sinn, H., *Recycling of plastics.* Conservation Recycling, 1976. **1**: p. 91-110.
37. Sinn, H.K., W.; Janning, J., *Plastic waste and scrap tires into chemical raw materials, especially by pyrolysis.* Angew. Chem. Int. Ed., 1976. **15**: p. 660-672.
38. Kaminsky, W.S., W.; Schwesinger, H., *Properties and decomposition of lignins, decomposition by pyrolysis in a fluidized bed.* Holzforschung, 1980. **34**: p. 73-76.
39. Kaminsky, W.K., A.B., *Fluidized bed pyrolysis of digested sewage sludge.* J. Anal. Appl. Pyrolysis, 1989. **16**: p. 27-35.
40. Predel, M.K., W., *Pyrolysis of rape-seed in a fluidized bed reactor.* Bioresource Technology, 1998. **66**: p. 113-117.
41. Arena, U.M., M.L., *Fluidized bed pyrolysis of plastic waste*. Feedstock recycling and pyrolysis of plastic waste, ed. J.K. Scheirs, W. 2005: J. Wiley & Sons. 435-474.
42. Scheirs, J., *Polymer recycling science, technology and application*. 1998, Chichester: John Wiley & Sons Ltd.
43. Mertinkat, J.K., A; Predel, M; Kaminsky, W., *Cracking catalyst used as fluidized bed material in the Hamburg pyrolysis process.* J. Anal. Appl. Pyrolysis, 1999. **49**: p. 87-95.
44. Predel, M.K., W., *Pyrolysis of mixed polyolefins in a fluidized bed reactor and on a Pyro-GC/MS to yield aliphatic waxes.* Polymer Degradation and Stability, 2000. **70**: p. 373-385.
45. Arena, U.M., M.L., *Defluidization phenomena during th pyrolysis of two plastic wastes* Chemical Engineering Science, 2000. **55**: p. 2849-2860.
46. Bez, J.N., T., *Feedstock recycling of plastic waste in the polymer cracking process of the BP-consortium*, in *Fraunhofer-Institut Final Report for APME*. 2001.
47. Kaminsky, W.S., B.; Simon, C.M., *Olefins from polyolefins and mixed plastics by pyrolysis.* J. Anal. Appl. Pyrolysis, 1995. **32**: p. 19-27.

48. Arena, U.M., M.L., *The phenomenology of bed defluidization during the pyrolysis of a food-packaging plastic waste.* Powder technology, 2001. **120**: p. 127-133.
49. Arena, U.M., M.L., *Fluidized bed pyrolysis of plastic waste*. Feedstock recycling and pyrolysis of plastic waste, ed. J.K. Scheirs, W. 2006: J. Wiley & Sons. 435-474.
50. Kaminsky, W., *Pyrolysis of Polymers*. Emerging Technologies in Plastics Recycling, ed. G.D.S. Andrews, P.M. 1992, Washington, DC: American Chemical Society. 60-72.
51. Malkow, T., *Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal.* Waste Management, 2004. **24**: p. 53-79.
52. Buekens, G.H., H, *Catalytic plastics cracking for recovery of gasoline range hydrocarbons from municipal plastic wastes.* Resources, Conversion and Recycling, 1998. **23**: p. 163-181.
53. Alexander and Rice, F.O.K., *Thermal Decomposition of Hydrocarbons, Resonance Stabilization and Isomerization of Free Radicals.* 1943. **65**: p. 591-595.
54. Kaminsky, W., *Thermal Recycling of Polymers.* J. Anal. Appl. Pyrolysis, 1985. **8**: p. 439-448.
55. Cullis, C.F.H.M.M., *The combustion of organic polymers*. Science Publications. 1981, Oxford. 93-129.
56. Aguado, J.S., D.P; Escola, J.M., *Catalytic upgrading of plastic wastes*. Feedstock Recycling and Pyrolysis of Waste Plastics, ed. J.K. Scheirs, W. 2006, Chichester: John Wiley & Sons. 73-110.
57. Walendziewsky, J., *Thermal and catalytic conversion of polyolefins*. Feedstock Recycling and Pyrolysis of Waste Plastics, ed. J.K. Scheirs, W. 2006, Chichester: John Wiley & Sons. 111-128.
58. Lee, K., *Thermal and catalytic degradation of waste HDPE*. Feedstock Recycling and Pyrolysis of Waste Plastics, ed. J.K. Scheirs, W. 2006, Chichester: Jonh Wiley & Sons. 129-160.
59. Manos, G., *Catalytic degradation of plastic waste to fule over microporous materials*. Feedstock Recycling and Pyrolysis of Waste Plastics, ed. J.K. Scheirs, W. 2006, Chichester: John Wiley & Sons. 193-208.
60. Yanik, J.K., T., *Liquefaction of municipal wste plastics over acidic and nonacidic catalysts*. Feedstock Recycling and Pyrolysis of Waste Plastics, ed. J.K. Scheirs, W. 2006, Chichester: John Wiley & Sons. 209-224.
61. Aguado, J.S., D.P; Escola, J.M.; Garagorri; E., *Catalytic conversion of low-density polyethylene usin a continuous screw kiln reactor.* Cat. Today, 2002. **75**: p. 257-262.
62. . Feedstock recycling and pyrolysis of waste plastics, ed. J.K. Scheirs, W. 2006, Chichester: John Wiley & Sons.
63. Dufaud V., B.J.M., *Katalytische Hydrogenolyse von Polyethylen und Polypropylen bei niedrigen Temperaturen und Drücken durch ein Zirconiumhydrid auf Alumokieselgel - ein Schritt in Richtung Polyolefin-Abbau durch Umkehr der Ziegler-Natta-Polymerisation.* Angew. Chem., 1998. **110**(848-852).

64. Dufaud V., B.J.M., *Katalytische Hydrogenolyse von Polyethylen und Polypropylen bei niedrigen Temperaturen und Drücken durch ein Zirconiumhydrid auf Alumokieselgel - ein Schritt in Richtung Polyolefin-Abbau durch Umkehr der Ziegler-Natta-Polymerisation.* Angew. Chem. Int. Ed., 1998. **37**: p. 806-810.
65. White, R., *Acid-catalyzed cracking of polyolefins: Primary reaction mechanism*. Feedstock recycling and pyrolysis of waste plastics, ed. J.K. Scheirs, W. 2006, Chichester: John Wiley & Sons. 45-72.
66. Masuda, T.T., T., *Development of a process for the continuous conversion of waste plastics mixtures to fuel*. Feedstock recycling and pyrolysis of waste plastics, ed. J.K. Scheirs, W. 2006, Chichester: John WIley & Sons. 161-192.
67. Manos, G., *Catalytic degradation of plastic waste to fuel over microporous materials*. Feedstock recycling and pyrolysis of waste plastics, ed. J.K. Scheirs, W. 2006, Chichester: John Wiley & Sons. 193-208.
68. Beltrame, P.C., P. , *Catalytic degradation of polymers :Part II – Degradation of polyethilene.* Polymer Degradation and Stability, 1989. **26**: p. 209-220.
69. Ng, S.H.S., H.; Stanciulescu, M.; Sugimoto, Y., *Conversion of polyethylene to transportation fuels through pyrolysis and catalytic cracking.* Energy and Fuels, 1995. **9**: p. 735-742.
70. Liu, K.M., H.C.L., *Catalytic reactions in waste plastics , HDPE and coal studied by high-pressure thermogravimetry with on-line GC/MS.* Fuel Proc. Tech. , 1996. **49**: p. 1-15.
71. Uemichi, Y.T., K.; Ayane, A. , *Chemical recycling of poly(ethylene) by catalytic degradation into aromatic hydrocarbons using H-Ga-silicate.* Chem. Commun., 1998: p. 1975-1976.
72. Pifer, A.S., A. , *Recycling von Kunststoffen durch oxidativen Abbau zu wertvollen organischen Verbindungen.* Angew. Chem., 1998. **110**: p. 3500-3502.
73. Conesa, J.A.M.-G., I.; Font, R.; Jauhiainen, J., *Complete Study of the Pyrolysis and Gasification of Scrap Tires in a Pilot Plant Reactor.* Environ. Sci. Technol, 2004. **38**: p. 3189-3194.
74. Schmidt, H.S., C.; Kaminsky, W., Macromol. Symp., 2000. **152**: p. 191.
75. Kim, J.S.K., W., J. Anal. Appl. Prolysis, 1999. **51**: p. 127.
76. Weber, S.B., C.; Berruti, F.; Chan, E.; Gray, M., *Agglomerate stability in fluidized beds of glass beads and silica sand.* Powder Technology, 2006. **165**: p. 115-127.
77. Cotton, F.A.W., G.; Murillo, C.A.; Bochmann, M. . Inorganic Chemistry. 1999: John Wiley & Sons.
78. Kiand, J.K.Y.U., P.C.; Chien, J.C.W., *Polymer reactions. 7. Thermal pyrolysis of polypropylene.* Polymer Degradation and Stability, 1980. **2**: p. 113-127.
79. Kruse, T.M.W., H.W.; Broadbelt, L.J., *Mechanistic modelling of polymer pyrolysis: Polypropylene.* Macromolecules, 2003. **36**: p. 9594-9607.
80. Industries, C., *Advanced recycling of plastics; A parametric study of the thermal depolymerization of plastics*, in *Final report with the American Plastics Council*. 1995.

81. Scheirs, J., *Overview of commercial pyrolysis processes for waste plastics*. Feedstock Recycling and Pyrolysis of Waste Plastics, ed. J.K. Scheirs, W. 2006, Chichester: John Wiley & Sons.
82. Madorsky, S.L.S., S., Ind. Eng. Chem., 1948. **5**: p. 848.
83. Wall, L.A.J., Res. Natl. Bur. Std., 1948. **41**: p. 315.
84. Bradt, P.D., V. H.; Mohler, F. L. J., Res. Natl. Bur. Std., 1953. **50**: p. 201.
85. James, A.T.M., A. J. P., Analyst, 1952. **77**: p. 915.
86. Golay, M.J.E., *Gas Chromatography.* 1958, New York: Academic Press.
87. Dandenau, R.Z., H. E. J., High Res. Chromatogr. Commun., 1979. **2**: p. 351.
88. Kaminsky, M.P.W., *Pyrolysis of mixed polyolefins in a fluidised-bed reactor and on a pyro-GC/MS to yield aliphatic waxes.* J. Anal. Appl. Pyrolysis, 2000. **70**: p. 373-385.
89. Blazsó, M., *Composition of liquid fuels derived from the pyrolysis of plastics*. Feedstock recycling and pyrolysis of plastic waste, ed. J.K. Scheirs, W. 2006: J. Wiley & Sons. 315-344.
90. Pinto, F.C., P.; Gulyurtly, I.; Cabrita, I., *Pyrolysis of plastics wastes. 1. Effect of plastic waste composition on product yield.* J. Anal. Appl.Pyrol., 1999. **51**(39-55).
91. Head, R.B., *The thermodynamic properties of the lower chlorides of titanium.* Australian Journal of Chemistry, 1960. **13**: p. 332-340.
92. Pike, F.P.F., C. T., Jr. , *Vaupor pressure and boiling point of titanium tetrachloride.* Journal of Chemical and Engineering Data, 1959. **4**: p. 305-306.
93. Chambers, C.L., J.W.; , *Polymer waste reclamation by pyrolysis in molten salts.* Ind. Eng. Chem. Process. Des. Dev., 1984. **23**: p. 648-654.
94. Ivanova, S.R.G., E.F.; Minsker, K.S.; Zaikov, G.E.; Berlin, A.A., *Selective Catalytic degradation of polyolefins.* Prog. Polym. Sci., 1990. **15**: p. 193-215.
95. Natta, G.P., P.; Corradini, P.; Danuso, D.; Mantica, E.; Mazzanti, G.; Moraglio, G. , J. Am. Chem. Soc., 1955. **77**: p. 1708.
96. Ziegler, K.H., E.; Breil, H.; Martin H., *German Patent 533362*. 1953.
97. van der Ven, S., *Polypropylene and other Polyolefins: Polymerization and Characterization*. 1990, B. V.: Elsevier Science Publishers.
98. Donner, M., *Synthese und Pyrolyse von metallocen-katalysierten Ethen/Norbonen-Copolymeren*, in *TMC*. 2006, University of Hamburg: Hamburg. p. 178.
99. Schlesselmann, B., *PhD thesis*, in *TMC*. 1997, University of Hamburg: Hamburg.
100. Jorgensen, A.D.P., K. C.; Stamoudis, K. C., *Prediction of Gas Chromatography Flame Ionization Detector Response Factors from Molecular Structures.* Anal. Chem., 1990. **62**: p. 683-689.
101. *BGBl*. 2005. p. 2618.
102. *BGBl*. 2004. p. 3758.
103. Merck, *Online Datenbank.* 2006.

10. APPENDIX

Table A.1.- Single product components (wt%) of the pyrolysis of PP without catalyst

	PR-I	
	WOC	
	400ºC	**500ºC**
Total input material (g)	10,00	10,00
wt % pyrolysed PP	57,50	100,00
wt % gas	10,00	20,56
wt % light oil fraction	12,10	62,21
Component (gas + light oil)		
Hydrogene	0,00	0,07
Methane	0,20	0,79
Ethane	0,56	1,89
Ethene	0,05	0,65
Propane	0,25	0,68
Propene	3,43	9,59
1-Butene	0,00	0,07
1,3-Butadiene	2,46	1,93
2-Methyl-propene	0,00	0,50
2-Butene	0,85	2,62
1-Pentene	0,07	0,27
2-Methyl-1-butene	0,00	0,14
2-Ethylbutane	0,04	0,00
2-Pentene	0,00	0,28
2-Methyl-2-butene	0,41	3,67
2,2-Dimethylpropane	0,03	0,05
Cis-2-hexene	1,04	0,98
4-Methyl-1-pentene	0,00	0,00
2-Methyl-1-pentene	0,10	5,60
2,3-Dimethyl-2-butene	0,08	0,32
3-Methyl-2-pentene	0,00	0,11
2-Methyl-2-pentene	0,00	0,00
2-Methyl-1,3-pentadiene	0,00	0,61
2,4-Hexadiene	0,00	0,37
C1-C6	**9,57**	**31,10**
2,4-Dimethyl-1-pentene	0,00	0,90
2,4-Dimethyl-2-pentene	0,00	1,18
3-Methylhexane	0,00	0,19
2-Methyl-1-hexene	0,03	0,10
2-Methyl-2-hexene	0,00	0,72
3-Methyl-2-hexene	0,00	0,07
3,4-Dimethyl-2-pentene	0,05	0,01
4,4-Dimethyl-2-hexene	0,01	0,23
2,5-Dimethyl-2-hexene	0,09	1,07
4-Methylheptane	0,29	1,53
3-Octene	0,05	0,00
3,3-Dimethyl-1-hexene	0,00	0,36
C7-C8	**0,52**	**6,36**
3-Methyl-4-methyleneheptane	0,08	0,44

2,4-Dimethylheptane	0,03	0,26
2,2-Dimethyl-3-heptene	0,21	0,31
2,3-Dimethyl-2-heptene	0,00	0,73
2,4-Dimethyl-1-heptene	4,27	24,88
2,6-Dimethyl-3-heptene	0,02	0,19
2-Methyl-3-octene	0,00	0,70
2,3-Dimethyl-2-heptene	0,08	0,11
C9	**4,69**	**27,62**
2,4,6-Trimethyl-1-heptene	0,01	0,12
3-Decene	0,01	0,08
2-Methyl-3-nonene	0,01	0,11
2,6-Dimethyl-2-octene	0,01	0,18
2,4,6-Trimethyl-3-heptene	0,02	0,09
2,3,4-Trimethylhexane	0,51	0,45
5-Ethyl-2,4-dimethyl-2-heptene	0,15	1,13
2,6-Dimethylnonane	0,10	0,30
4-Methyldecane	0,10	0,28
2,3,7-Trimethyl-2-octene	0,00	0,01
4-Dodecene	0,00	0,97
3-Methyl-3-undecene	0,33	1,48
7-Methyl-4-undecene	0,02	0,26
8-Methyl-4-undecene	0,02	0,18
2,4-Dimethyl-2-decene	0,01	0,15
7-Methyl-1-undecene	0,49	1,55
2,4-Dimethyl-4-decene	0,05	0,02
5-Methyl-3-undecene	0,12	0,11
2,2-Dimethyl-3-decene	0,61	0,64
6,6,8-Trimethyl-1-nonene	0,31	0,22
4,5-Dimethyl-2-undecene	0,03	0,22
C10-C13	**2,92**	**8,55**
wt % heavy oil fraction	35,40	17,24
wt % not pyrolysed PP	42,50	0,00

Table A.2.- Single product components (wt%) of the pyrolysis of PP using $TiCl_3$ as catalyst

	PR-I					
	$TiCl_3$					
	400ºC 0,1%	**500ºC 0,1%**	**400ºC 1%**	**500ºC 1%**	**400ºC 5%**	**500ºC 5%**
Total input material (g)	10,00	10,00	10,00	10,00	10,00	10,00
wt % pyrolysed PP	91,19	94,12	88,83	99,50	91,79	97,62
wt % gas	10,36	11,76	5,04	10,89	3,53	19,05
wt % light oil fraction	61,20	57,77	68,66	53,85	75,52	46,90
Component (gas + light oil)						
Hydrogene	0,00	0,05	0,04	0,19	0,21	0,23
Methane	1,18	0,41	0,17	6,84	0,08	0,56
Ethane	2,24	0,74	0,38	0,51	0,18	0,68
Ethene	0,39	0,27	0,06	0,22	0,05	0,43
Propane	0,81	0,33	0,23	0,22	0,13	0,89
Propene	10,29	3,74	1,85	1,88	1,09	3,49
1-Butene	2,20	0,06	0,04	0,01	0,02	1,99
1,3-Butadiene	0,00	1,97	0,86	0,23	0,47	0,36

2-Methyl-propene	0,23	0,69	0,19	0,64	1,17	0,19
2-Butene	3,79	1,35	0,59	0,57	1,69	3,22
1-Pentene	0,00	0,26	0,06	0,05	0,10	0,52
2-Methyl-1-butene	0,00	0,32	0,00	0,03	0,10	1,19
2-Ethylbutane	0,01	0,00	0,02	0,03	0,16	0,71
2-Pentene	0,48	0,84	0,37	0,82	2,57	1,53
2-Methyl-2-butene	3,32	3,73	3,42	3,34	5,26	1,98
2,2-Dimethylpropane	0,00	0,07	0,02	0,01	0,42	0,49
Cis-2-hexene	0,00	0,59	0,37	0,09	0,23	0,41
4-Methyl-1-pentene	0,01	0,05	0,04	0,14	0,39	0,27
2-Methyl-1-pentene	4,94	5,39	4,09	3,65	1,95	1,17
2,3-Dimethyl-2-butene	0,30	0,33	1,03	0,70	2,30	1,55
3-Methyl-2-pentene	0,03	0,02	0,04	0,16	0,62	0,39
2-Methyl-2-pentene	0,01	0,05	0,04	0,06	0,33	0,25
2-Methyl-1,3-pentadiene	0,32	0,60	0,47	0,65	0,14	0,06
2,4-Hexadiene	0,10	0,32	0,22	0,47	0,30	0,20
C1-C6	**30,63**	**22,13**	**14,57**	**21,35**	**19,76**	**22,53**
2,4-Dimethyl-1-pentene	0,48	0,78	0,63	1,08	0,74	0,76
2,4-Dimethyl-2-pentene	0,58	0,99	0,67	0,79	1,50	1,02
3-Methylhexane	0,03	0,03	0,05	0,12	0,27	0,32
2-Methyl-1-hexene	0,13	0,19	0,10	0,24	0,17	0,04
2-Methyl-2-hexene	0,04	0,45	0,94	1,03	2,41	0,70
3-Methyl-2-hexene	0,01	0,05	0,04	0,07	0,33	0,31
3,4-Dimethyl-2-pentene	0,02	0,01	0,05	0,05	0,35	0,28
4,4-Dimethyl-2-hexene	0,07	0,03	0,03	0,02	0,29	0,33
2,5-Dimethyl-2-hexene	0,01	0,04	0,30	0,09	0,58	0,49
4-Methylheptane	1,31	1,08	1,84	0,07	2,57	0,56
3-Octene	0,01	0,04	0,01	0,12	0,80	0,33
3,3-Dimethyl-1-hexene	0,24	0,01	0,29	0,05	0,04	0,44
C7-C8	**2,94**	**3,69**	**4,94**	**3,73**	**10,04**	**5,58**
3-Methyl-4-methyleneheptane	0,38	0,01	0,49	0,06	0,88	0,36
2,4-Dimethylheptane	0,13	0,13	0,23	0,20	0,46	0,29
2,2-Dimethyl-3-heptene	0,10	0,23	1,16	0,39	0,59	0,32
2,3-Dimethyl-2-heptene	0,79	0,60	3,27	0,31	0,75	0,49
2,4-Dimethyl-1-heptene	21,83	19,72	23,51	16,94	16,21	6,55
2,6-Dimethyl-3-heptene	0,02	0,02	1,89	0,30	0,97	0,76
2-Methyl-3-octene	0,03	0,04	0,33	0,05	0,27	0,23
2,3-Dimethyl-2-heptene	0,11	0,88	0,40	0,01	0,26	0,22
C9	**23,39**	**21,63**	**31,28**	**18,26**	**20,41**	**9,21**
2,4,6-Trimethyl-1-heptene	0,02	0,01	0,17	0,02	0,22	0,24
3-Decene	0,05	0,06	0,08	0,16	0,32	0,20
2-Methyl-3-nonene	0,02	0,02	0,02	0,08	0,24	0,06
2,6-Dimethyl-2-octene	0,04	0,08	0,14	0,16	0,29	0,37
2,4,6-Trimethyl-3-heptene	0,03	0,09	0,60	0,17	0,20	0,38
2,3,4-Trimethylhexane	0,03	0,97	0,42	0,06	0,00	0,04
5-Ethyl-2,4-dimethyl-2-heptene	0,11	0,02	1,12	0,36	1,85	1,36
2,6-Dimethylnonane	0,24	0,24	0,70	0,25	0,03	0,09
4-Methyldecane	0,23	0,24	0,66	0,21	0,08	0,14
2,3,7-Trimethyl-2-octene	0,00	0,01	0,23	0,02	0,06	0,21
4-Dodecene	0,27	0,04	0,11	0,07	0,73	0,08
3-Methyl-3-undecene	1,35	1,01	0,55	0,22	0,40	0,25
7-Methyl-4-undecene	0,74	0,01	0,30	1,24	0,53	0,23
8-Methyl-4-undecene	0,05	0,07	0,02	0,14	0,17	0,06
2,4-Dimethyl-2-decene	0,02	0,06	0,41	0,13	0,10	0,18

7-Methyl-1-undecene	0,50	1,63	2,32	1,12	0,07	0,06
2,4-Dimethyl-4-decene	0,02	0,01	0,08	0,08	0,07	0,05
5-Methyl-3-undecene	0,05	0,01	0,12	0,03	0,03	0,03
2,2-Dimethyl-3-decene	0,00	0,04	0,17	0,02	0,05	0,15
6,6,8-Trimethyl-1-nonene	0,04	1,31	0,58	0,09	0,00	0,04
4,5-Dimethyl-2-undecene	0,01	0,01	0,08	0,00	0,00	0,04
C10-C13	**3,81**	**5,93**	**8,86**	**4,63**	**5,42**	**4,27**
wt % heavy oil fraction	19,63	24,58	15,13	34,76	12,73	31,67
wt % not pyrolysed PP	8,81	5,88	11,17	0,50	8,21	2,38

Table A.3.- Single product components (wt%) of the pyrolysis of PP using $TiCl_4$ as catalyst

	PR-I					
	$TiCl_4$					
	400ºC 0,1%	**500ºC 0,1%**	**400ºC 1%**	**500ºC 1%**	**400ºC 5%**	**500ºC 5%**
Total input material (g)	10,00	10,00	10,00	10,00	10,00	10,00
wt % pyrolysed PP	94,77	99,33	98,39	98,67	95,26	99,05
wt % gas	5,42	3,14	7,51	5,81	7,20	0,76
wt % light oil fraction	77,02	75,35	70,94	49,39	55,08	53,91
Component (gas + light oil)						
Hydrogene	0,22	0,37	0,12	0,19	0,54	0,60
Methane	0,61	0,31	0,48	0,47	1,06	0,09
Ethane	0,56	0,32	0,54	0,43	0,67	0,08
Ethene	0,09	0,12	0,05	0,10	0,08	0,03
Propane	0,18	0,10	0,40	0,25	0,53	0,05
Propene	3,35	2,52	4,05	1,96	2,90	0,44
1-Butene	0,01	0,01	0,04	0,03	0,05	0,01
1,3-Butadiene	0,54	0,27	0,60	0,65	0,64	0,05
2-Methyl-propene	0,81	1,08	0,38	0,07	0,08	0,10
2-Butene	0,45	0,34	0,61	0,56	0,72	0,14
1-Pentene	0,00	0,13	2,23	0,91	0,22	0,01
2-Methyl-1-butene	0,26	0,03	0,06	0,07	0,09	0,01
2-Ethylbutane	0,03	0,00	0,00	0,00	0,01	0,00
2-Pentene	0,46	0,66	0,61	0,32	0,55	0,56
2-Methyl-2-butene	5,28	5,42	9,60	3,19	7,20	7,73
2,2-Dimethylpropane	0,00	0,07	0,21	0,06	0,00	0,02
Cis-2-hexene	0,00	0,00	0,00	0,00	0,00	0,00
4-Methyl-1-pentene	0,02	0,05	0,08	0,05	0,04	0,03
2-Methyl-1-pentene	6,61	6,35	1,80	0,95	1,02	1,78
2,3-Dimethyl-2-butene	0,49	0,46	4,23	1,08	0,10	0,13
3-Methyl-2-pentene	0,04	0,07	0,04	0,02	0,08	0,16
2-Methyl-2-pentene	0,52	0,06	0,06	0,03	0,00	0,01
2-Methyl-1,3-pentadiene	0,14	0,62	0,02	0,01	0,00	0,01
2,4-Hexadiene	0,58	0,28	0,60	0,32	0,01	0,03
C1-C6	**21,04**	**19,26**	**26,72**	**11,52**	**16,06**	**11,49**
2,4-Dimethyl-1-pentene	0,04	0,74	0,08	0,03	0,02	0,03
2,4-Dimethyl-2-pentene	0,79	0,93	0,95	0,43	0,06	0,01
3-Methylhexane	0,01	0,04	0,06	0,03	0,04	0,02
2-Methyl-1-hexene	0,15	0,17	0,00	0,01	0,01	0,03
2-Methyl-2-hexene	0,42	0,47	0,33	0,20	0,07	0,44
3-Methyl-2-hexene	0,04	0,05	0,03	0,05	0,04	0,27

3,4-Dimethyl-2-pentene	0,01	0,02	0,00	0,02	0,02	0,04
4,4-Dimethyl-2-hexene	0,10	0,08	0,04	0,05	0,02	0,04
2,5-Dimethyl-2-hexene	0,23	0,31	0,43	0,29	0,30	0,39
4-Methylheptane	0,28	0,33	0,34	0,27	0,08	0,12
3-Octene	0,37	0,02	0,29	0,19	0,03	0,04
3,3-Dimethyl-1-hexene	0,38	0,52	0,71	0,50	0,15	0,15
C7-C8	**2,83**	**3,67**	**3,25**	**2,05**	**0,84**	**1,57**
3-Methyl-4-methyleneheptane	0,51	0,01	0,49	0,25	0,03	0,38
2,4-Dimethylheptane	0,15	0,14	0,40	0,24	0,27	0,90
2,2-Dimethyl-3-heptene	1,17	0,88	1,08	0,51	0,57	0,83
2,3-Dimethyl-2-heptene	0,05	0,05	0,21	0,12	0,62	0,62
2,4-Dimethyl-1-heptene	22,13	22,13	16,86	11,55	2,23	2,17
2,6-Dimethyl-3-heptene	0,17	0,03	0,35	0,21	0,31	1,00
2-Methyl-3-octene	0,01	0,07	0,06	0,01	0,05	0,14
2,3-Dimethyl-2-heptene	0,17	0,21	0,38	0,73	0,13	0,15
C9	**24,36**	**23,53**	**19,83**	**13,62**	**4,21**	**6,20**
2,4,6-Trimethyl-1-heptene	0,52	0,60	0,03	0,04	0,03	0,02
3-Decene	0,09	0,07	0,06	0,07	0,02	0,09
2-Methyl-3-nonene	0,09	0,01	0,07	0,03	0,01	0,11
2,6-Dimethyl-2-octene	0,01	0,02	0,04	0,06	0,01	0,01
2,4,6-Trimethyl-3-heptene	0,16	0,15	0,91	0,75	1,17	0,81
2,3,4-Trimethylhexane	2,86	2,27	0,51	0,52	1,30	0,10
5-Ethyl-2,4-dimethyl-2-heptene	0,27	0,30	0,53	0,34	0,94	0,83
2,6-Dimethylnonane	0,53	0,40	0,93	0,77	1,11	0,93
4-Methyldecane	0,53	0,40	0,67	0,39	0,69	0,58
2,3,7-Trimethyl-2-octene	0,18	0,18	1,71	1,78	1,43	0,41
4-Dodecene	0,07	0,01	0,05	0,05	0,02	0,03
3-Methyl-3-undecene	1,96	1,53	1,48	0,77	0,77	0,04
7-Methyl-4-undecene	0,85	0,97	1,06	0,46	0,11	0,11
8-Methyl-4-undecene	0,09	0,08	0,07	0,02	0,04	0,03
2,4-Dimethyl-2-decene	0,10	0,10	0,65	0,48	0,43	0,20
7-Methyl-1-undecene	2,76	2,53	1,19	0,90	0,11	0,33
2,4-Dimethyl-4-decene	0,02	0,01	0,33	0,40	0,62	0,47
5-Methyl-3-undecene	0,05	0,04	0,41	0,41	0,54	0,62
2,2-Dimethyl-3-decene	3,48	2,91	1,49	1,43	1,24	0,22
6,6,8-Trimethyl-1-nonene	1,95	1,33	0,63	0,61	0,28	1,13
4,5-Dimethyl-2-undecene	0,06	0,04	0,03	0,05	0,19	0,34
C10-C13	**16,60**	**13,95**	**12,85**	**10,34**	**11,05**	**7,40**
wt % heavy oil fraction	12,33	20,84	19,94	43,47	32,97	44,38
wt % not pyrolysed PP	5,23	0,67	1,61	1,33	4,74	0,95

Table A.4.- Single product components (wt%) of the pyrolysis of PP using $AlCl_3$ as catalyst

	PR-I										
	$AlCl_3$										
	300ºC 0,1%	**400ºC 0,1%**	**500ºC 0,1%**	**250ºC 1%**	**300ºC 1%**	**400ºC 1%**	**500ºC 1%**	**250ºC 5%**	**300ºC 5%**	**400ºC 5%**	**500ºC 5%**
Total input material (g)	10,00	10,00	10,00	10,00	10,00	10,00	10,00	10,00	10,00	10,00	10,00
wt % pyrolysed PP	3,60	95,50	99,40	8,12	68,42	96,44	97,82	30,58	76,35	98,48	96,11
wt % gas	0,70	2,20	4,40	3,86	0,69	9,21	7,43	16,81	15,57	10,35	7,03
wt % light oil fraction	0,87	72,47	62,65	1,28	55,83	80,10	76,51	4,13	41,72	76,39	68,15
Component (gas + light oil)											
Hydrogene	0,00	0,05	0,20	0,00	0,25	0,90	0,65	0.96	0,01	0,74	5,64
Methane	0,00	0,10	0,35	0,00	0,02	0,92	0,07	0,00	0,04	0,04	0,21
Ethane	0,02	0,16	0,38	0,00	0,01	0,33	0,03	0,00	0,04	0,01	0,04
Ethene	0,00	0,02	0,11	0,00	0,00	0,11	0,01	0,00	0,03	0,00	0,03
Propane	0,01	0,07	0,16	0,04	0,02	0,40	0,02	0,01	0,32	0,02	0,05
Propene	0,10	2,03	3,42	0,04	2,52	6,66	0,56	0,01	3,22	0,43	0,67
1-Butene	0,03	0,01	0,01	1,00	0,16	1,23	0,01	0,19	5,41	0,23	0,52
1,3-Butadiene	0,23	0,37	0,55	0,01	0,01	0,51	0,02	0,15	3,35	0,12	0,01
2-Methyl-propene	0,00	0,03	0,06	0,00	0,49	1,55	0,46	0,00	0,09	4,78	2,81
2-Butene	0,05	0,97	1,49	0,04	2,29	4,39	2,55	0,03	3,46	8,72	6,55
1-Pentene	0,02	0,03	0,05	0,02	0,01	0,15	0,00	0,00	0,18	0,01	0,01
2-Methyl-1-butene	0,01	0,01	0,02	0,06	0,03	0,36	0,00	0,01	0,38	0,01	0,02
2-Ethylbutane	0,00	0,00	0,00	0,00	0,07	0,14	0,09	0,00	0,00	0,02	0,16
2-Pentene	0,01	0,40	0,71	0,02	0,45	0,88	0,64	0,00	0,18	0,40	0,55
2-Methyl-2-butene	0,08	5,17	4,94	0,12	3,03	7,56	5,76	0,02	2,61	1,82	2,49
2,2-Dimethylpropane	0,00	0,01	0,03	0,00	0,05	0,00	0,03	0,00	0,00	0,00	0,02
Cis-2-hexene	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
4-Methyl-1-pentene	0,00	0,02	0,04	0,00	0,07	0,13	0,15	0,00	0,00	0,00	0,00
2-Methyl-1-pentene	0,02	5,60	5,16	0,02	2,00	3,41	2,06	0,25	3,54	7,45	6,53
2,3-Dimethyl-2-butene	0,00	0,44	0,60	0,00	0,97	2,55	2,57	0,01	0,00	0,49	0,62
3-Methyl-2-pentene	0,00	0,01	0,03	0,00	0,63	1,02	0,73	0,00	0,48	0,84	0,10

2-Methyl-2-pentene	0,00	0,47	0,51	0,00	0,42	0,43	0,25	0,05	0,03	0,08	0,03
2-Methyl-1,3-pentadiene	0,00	0,15	0,24	0,00	0,25	0,44	0,33	0,01	0,00	0,00	0,75
2,4-Hexadiene	0,00	0,56	0,60	0,00	0,02	0,03	0,17	0,00	0,00	0,02	0,13
C1-C6	**0,59**	**16,66**	**19,47**	**1,40**	**13,53**	**33,21**	**16,53**	**0,74**	**23,37**	**25,48**	**22,31**
2,4-Dimethyl-1-pentene	0,00	0,05	0,02	0,00	0,12	0,28	0,49	0,00	0,01	0,08	0,01
2,4-Dimethyl-2-pentene	0,00	0,73	0,69	0,00	0,27	0,68	1,07	0,01	0,03	0,12	0,27
3-Methylhexane	0,00	0,04	0,04	0,00	0,76	0,86	0,48	0,16	1,27	2,13	1,72
2-Methyl-1-hexene	0,00	0,14	0,00	0,00	0,15	0,22	0,24	0,00	0,16	0,09	0,20
2-Methyl-2-hexene	0,00	0,39	0,53	0,01	1,77	2,35	2,15	0,21	1,48	2,95	2,62
3-Methyl-2-hexene	0,00	0,02	0,01	0,00	0,40	0,52	0,40	0,00	0,00	0,11	0,15
3,4-Dimethyl-2-pentene	0,00	0,00	0,01	0,00	0,31	0,47	0,35	0,01	0,01	0,28	0,08
4,4-Dimethyl-2-hexene	0,00	0,06	0,02	0,00	0,50	0,54	0,46	0,01	0,03	0,27	0,46
2,5-Dimethyl-2-hexene	0,01	0,28	0,28	0,01	0,58	0,91	0,68	0,15	1,06	1,63	0,59
4-Methylheptane	0,00	1,14	1,23	0,00	0,67	0,81	0,95	0,06	0,45	0,74	0,15
3-Octene	0,00	0,32	0,27	0,00	0,54	0,56	0,47	0,01	0,08	0,30	0,10
3,3-Dimethyl-1-hexene	0,00	0,37	0,40	0,00	0,55	0,75	1,07	0,08	0,58	0,90	0,53
C7-C8	**0,02**	**3,55**	**3,50**	**0,03**	**6,63**	**8,96**	**8,81**	**0,71**	**5,15**	**9,60**	**6,87**
3-Methyl-4-methyleneheptane	0,01	0,45	0,35	0,01	0,57	0,68	0,56	0,00	0,13	0,31	0,37
2,4-Dimethylheptane	0,02	0,15	0,14	0,03	0,18	0,04	0,15	0,01	0,11	0,18	0,13
2,2-Dimethyl-3-heptene	0,02	0,96	0,71	0,02	0,22	0,45	0,36	0,04	0,28	0,43	0,48
2,3-Dimethyl-2-heptene	0,00	0,05	0,05	0,00	0,24	0,07	0,10	0,01	0,04	0,08	0,06
2,4-Dimethyl-1-heptene	0,02	22,44	19,94	0,03	1,55	3,57	7,47	0,24	1,65	2,58	3,05
2,6-Dimethyl-3-heptene	0,00	0,02	0,03	0,00	0,12	0,57	2,36	0,00	0,02	0,06	0,41
2-Methyl-3-octene	0,00	0,05	0,03	0,00	0,88	0,57	0,48	0,14	0,98	1,43	1,14
2,3-Dimethyl-2-heptene	0,00	0,14	0,15	0,00	0,16	0,15	0,09	0,00	0,05	0,07	0,05
C9	**0,07**	**24,26**	**21,41**	**0,10**	**3,93**	**6,10**	**11,57**	**0,44**	**3,26**	**5,13**	**5,68**
2,4,6-Trimethyl-1-heptene	0,00	0,03	0,02	0,00	0,47	0,47	0,12	0,07	0,52	0,75	0,59
3-Decene	0,00	0,05	0,01	0,00	0,14	0,41	0,17	0,03	0,34	0,62	0,57
2-Methyl-3-nonene	0,00	0,07	0,08	0,00	0,23	0,19	0,44	0,04	0,33	0,48	0,33
2,6-Dimethyl-2-octene	0,00	0,04	0,03	0,00	0,26	0,23	0,16	0,02	0,21	0,29	0,21
2,4,6-Trimethyl-3-heptene	0,01	0,16	0,10	0,02	0,15	0,17	0,17	0,02	0,18	0,27	0,21
2,3,4-Trimethylhexane	0,01	2,81	1,65	0,01	0,03	0,03	0,07	0,00	0,01	0,05	0,01
5-Ethyl-2,4-dimethyl-2-heptene	0,01	0,25	0,02	0,01	0,28	0,69	1,01	0,01	0,09	0,16	0,39

2,6-Dimethylnonane	0,02	0,44	0,36	0,02	0,19	0,32	0,13	0,01	0,20	0,28	0,25
4-Methyldecane	0,01	0,44	0,35	0,02	0,26	0,18	0,29	0,03	0,30	0,48	0,34
2,3,7-Trimethyl-2-octene	0,01	0,18	0,13	0,02	0,14	0,24	0,73	0,02	0,09	0,17	0,19
4-Dodecene	0,00	0,06	0,07	0,00	0,17	0,15	0,16	0,01	0,03	0,09	0,13
3-Methyl-3-undecene	0,02	1,59	1,17	0,03	0,10	0,42	0,54	0,02	0,23	0,49	0,55
7-Methyl-4-undecene	0,00	0,88	0,87	0,00	0,32	0,29	0,32	0,01	0,09	0,21	0,23
8-Methyl-4-undecene	0,00	0,07	0,03	0,00	0,41	0,29	0,22	0,06	0,53	0,76	0,60
2,4-Dimethyl-2-decene	0,00	0,10	0,03	0,01	0,20	0,11	0,11	0,02	0,15	0,42	0,24
7-Methyl-1-undecene	0,00	2,47	2,12	0,00	0,14	0,15	0,66	0,02	0,18	0,29	0,08
2,4-Dimethyl-4-decene	0,01	0,03	0,01	0,01	0,13	0,16	0,22	0,00	0,06	0,10	0,15
5-Methyl-3-undecene	0,01	0,04	0,01	0,01	0,52	0,46	0,20	0,06	0,50	0,76	0,40
2,2-Dimethyl-3-decene	0,01	3,47	2,21	0,01	0,06	0,20	0,55	0,00	0,02	0,07	0,04
6,6,8-Trimethyl-1-nonene	0,03	1,67	0,91	0,04	0,14	0,03	0,13	0,01	0,02	0,06	0,05
4,5-Dimethyl-2-undecene	0,00	0,03	0,04	0,00	0,07	0,04	0,16	0,00	0,09	0,18	0,69
C10-C13	**0,15**	**14,87**	**10,21**	**0,22**	**4,41**	**5,23**	**6,56**	**0,46**	**4,17**	**6,99**	**6,25**
wt % heavy oil fraction	2,03	20,83	32,36	2,98	11,90	7,13	13,88	9,64	19,06	11,73	20,93
wt % not pyrolysed PP	96,40	4,50	0,60	91,88	31,58	3,56	2,18	69,42	23,65	1,52	3,89

Table A.5.- Single product components (wt%) of the pyrolysis of PP using $TiCl_4$:$AlCl_3$ as catalyst

	$TiCl_4$:$AlCl_3$							
	1:1			**1:5**			**5:1**	
	250ºC 5%	**300ºC 5%**	**400ºC 5%**	**300ºC 1%**	**250ºC 5%**	**300ºC 5%**	**250ºC 5%**	**300ºC 5%**
Total input material (g)	10,00	10,00	10,00	10,00	10,00	10,00	10,00	10,00
wt % pyrolysed PP	20,70	88,98	89,93	24,26	36,09	49,67	15,29	38,94
wt % gas	0,57	26,12	24,79	7,62	9,59	0,09	0,38	2,37
wt % light oil fraction	15,27	47,07	60,81	4,99	21,11	47,25	11,18	20,00
Component (gas + light oil)								
Hydrogene	0,00	0,05	0,11	0,00	0,00	0,03	0,00	0,00

Methane	0,00	0,12	0,28	0,00	0,02	0,00	0,00	0,01
Ethane	0,00	0,09	0,26	0,01	0,02	0,00	0,00	0,01
Ethene	0,01	0,63	0,09	0,08	0,13	0,00	0,01	0,04
Propane	0,00	1,14	0,63	0,14	0,04	0,00	0,00	0,06
Propene	0,20	7,91	1,87	2,20	2,73	0,05	0,12	0,59
1-Butene	0,01	0,36	4,57	0,08	0,10	0,00	0,00	0,02
1,3-Butadiene	0,00	0,32	3,15	0,06	0,02	0,00	0,00	0,09
2-Methyl-propene	0,09	1,36	1,59	0,05	0,50	1,30	0,05	0,19
2-Butene	1,83	8,86	5,12	2,17	5,73	4,15	0,61	1,85
1-Pentene	0,00	0,04	0,58	0,02	0,03	0,00	0,00	0,00
2-Methyl-1-butene	0,05	1,42	1,79	0,65	1,03	0,01	0,04	0,19
2-Ethylbutane	0,01	0,14	0,20	0,01	0,00	0,15	0,02	0,00
2-Pentene	0,75	1,61	0,97	0,41	0,63	0,55	0,31	0,15
2-Methyl-2-butene	1,67	1,39	7,16	0,19	0,23	1,67	0,11	0,48
2,2-Dimethylpropane	0,27	0,35	0,13	0,00	0,00	0,00	0,03	0,01
Cis-2-hexene	0,00	0,00	0,00	0,02	0,02	0,00	0,00	0,00
4-Methyl-1-pentene	0,32	0,16	0,11	0,00	0,00	0,02	0,14	0,28
2-Methyl-1-pentene	1,76	2,32	2,60	0,33	3,44	3,92	0,80	1,73
2,3-Dimethyl-2-butene	0,06	0,16	0,59	0,02	0,05	0,14	0,06	0,11
3-Methyl-2-pentene	0,26	0,23	0,31	0,02	0,00	0,02	0,00	0,25
2-Methyl-2-pentene	0,03	0,33	0,37	0,05	0,49	0,57	0,15	0,03
2-Methyl-1,3-pentadiene	0,00	0,00	0,15	0,00	0,00	0,00	0,00	0,00
2,4-Hexadiene	0,00	0,03	0,05	0,00	0,00	0,00	0,00	0,00
C1-C6	**7,33**	**28,96**	**32,57**	**6,53**	**15,21**	**12,56**	**2,45**	**6,09**
2,4-Dimethyl-1-pentene	0,01	0,06	0,07	0,00	0,00	0,02	0,00	0,01
2,4-Dimethyl-2-pentene	0,01	0,10	0,18	0,01	0,00	0,05	0,03	0,00
3-Methylhexane	0,70	1,21	0,89	0,12	1,28	1,44	0,53	0,66
2-Methyl-1-hexene	0,05	0,06	0,12	0,01	0,12	0,16	0,06	0,06
2-Methyl-2-hexene	0,90	1,93	2,46	0,19	1,47	1,93	0,66	0,91
3-Methyl-2-hexene	0,02	0,24	0,29	0,01	0,01	0,05	0,00	0,07
3,4-Dimethyl-2-pentene	0,07	0,12	0,12	0,02	0,17	0,23	0,06	0,07
4,4-Dimethyl-2-hexene	0,01	0,07	0,04	0,00	0,04	0,15	0,00	0,02
2,5-Dimethyl-2-hexene	0,45	0,71	0,66	0,08	0,90	1,28	0,15	0,47

4-Methylheptane	0,43	1,08	0,93	0,11	0,91	1,40	0,53	0,52
3-Octene	0,00	0,17	0,17	0,01	0,02	0,21	0,36	0,02
3,3-Dimethyl-1-hexene	0,17	0,75	0,35	0,06	0,33	0,75	0,36	0,27
C7-C8	**2,83**	**6,51**	**6,30**	**0,63**	**5,25**	**7,67**	**2,74**	**3,07**
3-Methyl-4-methyleneheptane	0,01	0,14	0,43	0,00	0,02	0,00	0,03	0,06
2,4-Dimethylheptane	0,02	0,06	0,24	0,01	0,05	0,11	0,04	0,07
2,2-Dimethyl-3-heptene	0,08	0,22	0,25	0,02	0,19	0,30	0,15	0,13
2,3-Dimethyl-2-heptene	0,02	0,03	0,05	0,00	0,02	0,04	0,08	0,02
2,4-Dimethyl-1-heptene	0,47	1,58	1,69	0,16	1,11	2,00	0,71	0,64
2,6-Dimethyl-3-heptene	0,02	0,22	0,09	0,02	0,03	0,11	0,03	0,08
2-Methyl-3-octene	0,18	1,21	0,52	0,07	0,61	1,22	0,52	0,25
2,3-Dimethyl-2-heptene	0,02	0,02	0,14	0,01	0,03	0,11	0,05	0,05
C9	**0,83**	**3,48**	**3,41**	**0,30**	**2,05**	**3,90**	**1,60**	**1,29**
2,4,6-Trimethyl-1-heptene	0,10	0,62	0,50	0,05	0,14	0,58	0,03	0,19
3-Decene	0,06	0,43	0,17	0,04	0,05	0,37	0,12	0,14
2-Methyl-3-nonene	0,58	0,30	0,21	0,04	0,04	0,25	0,13	0,15
2,6-Dimethyl-2-octene	0,06	0,39	0,55	0,04	0,05	0,37	0,12	0,13
2,4,6-Trimethyl-3-heptene	0,01	0,16	0,05	0,02	0,01	0,21	0,09	0,07
2,3,4-Trimethylhexane	0,02	0,00	0,10	0,01	0,00	0,01	0,03	0,01
5-Ethyl-2,4-dimethyl-2-heptene	0,02	0,09	0,26	0,01	0,04	0,07	0,05	0,04
2,6-Dimethylnonane	0,02	0,08	0,22	0,02	0,01	0,27	0,09	0,07
4-Methyldecane	0,04	0,31	0,35	0,03	0,02	0,37	0,11	0,19
2,3,7-Trimethyl-2-octene	0,06	0,00	0,12	0,00	0,00	0,10	0,00	0,01
4-Dodecene	0,01	0,15	0,08	0,01	0,02	0,07	0,11	0,03
3-Methyl-3-undecene	0,06	0,29	0,43	0,03	0,14	0,27	0,12	0,19
7-Methyl-4-undecene	0,00	0,04	0,22	0,01	0,01	0,05	0,06	0,02
8-Methyl-4-undecene	0,09	0,59	0,45	0,05	0,12	0,58	0,16	0,19
2,4-Dimethyl-2-decene	0,02	0,04	0,20	0,02	0,01	0,20	0,06	0,08
7-Methyl-1-undecene	0,00	0,13	0,10	0,03	0,01	0,22	0,10	0,09
2,4-Dimethyl-4-decene	0,01	0,04	0,11	0,01	0,00	0,04	0,00	0,04
5-Methyl-3-undecene	0,05	0,18	0,60	0,05	0,01	0,33	0,12	0,16
2,2-Dimethyl-3-decene	0,00	0,00	0,02	0,01	0,00	0,06	0,00	0,00
6,6,8-Trimethyl-1-nonene	0,04	0,00	0,12	0,02	0,00	0,04	0,00	0,01

4,5-Dimethyl-2-undecene	0,07	0,30	0,19	0,08	0,01	0,57	0,07	0,24
C10-C13	**1,33**	**4,16**	**5,05**	**0,58**	**0,66**	**5,05**	**1,57**	**2,03**
wt % heavy oil fraction	4,86	15,80	4,34	11,64	5,39	2,32	3,73	16,56
wt % not pyrolysed PP	79,30	11,02	10,07	75,74	63,91	50,33	84,71	61,06

Table A.6.- Single product components (wt%) of the pyrolysis of PP in LWS-V

	LWS-V						
	$TiCl_3$	$TiCl_4$	$AlCl_3$		$TiCl_4$:$AlCl_3$ 1:1		
	400ºC 1%	400ºC 1%	300ºC 1%	400ºC 1%	300ºC 5%	350ºC 5%	400ºC 5%
Total input material (g)	3030,00	3000,00	2024,00	1010,00	910,00	952,00	1415,00
wt % pyrolysed PP	97,90	99,75	24,04	87,03	26,48	84,98	98,80
wt % gas	0,00	8,75	0,00	0,00	0,00	0,00	0,00
wt % light oil fraction	55,91	59,53	8,88	43,87	19,77	64,57	65,10
Component (gas + light oil)							
Hydrogene	1,68	1,09	0,00	0,00	0,00	0,00	0,00
Methane	0,00	0,45	0,00	0,00	0,00	0,00	0,00
Ethane	0,00	0,55	0,00	0,00	0,00	0,00	0,00
Ethene	0,00	0,21	0,00	0,00	0,00	0,00	0,00
Propane	0,00	0,33	0,00	0,00	0,00	0,00	0,00
Propene	0,28	3,19	0,00	0,32	0,00	0,11	0,36
1-Butene	0,00	0,13	0,00	0,00	0,00	0,00	0,00
1,3-Butadiene	0,00	0,55	0,00	0,00	0,00	0,00	0,00
2-Methyl-propene	0,99	1,14	0,00	0,08	0,14	0,60	1,46
2-Butene	0,28	2,00	0,00	0,41	0,78	1,92	3,73
1-Pentene	0,00	0,02	0,00	0,00	0,00	0,00	0,00
2-Methyl-1-butene	0,00	0,07	0,00	0,00	0,00	0,00	0,00
2-Ethylbutane	0,00	0,00	0,00	0,05	0,00	1,13	0,09
2-Pentene	0,22	0,73	0,00	0,19	0,17	0,40	0,01
2-Methyl-2-butene	5,88	5,19	0,09	2,56	0,42	2,83	2,93
2,2-Dimethylpropane	0,10	0,30	0,00	0,01	0,02	0,18	0,20
Cis-2-hexene	0,00	0,00	0,00	0,00	0,00	0,00	0,00
4-Methyl-1-pentene	0,17	0,19	0,01	0,01	0,21	0,28	0,05
2-Methyl-1-pentene	1,97	1,19	0,05	0,99	1,11	0,66	1,25
2,3-Dimethyl-2-butene	1,86	2,29	0,02	1,44	0,19	1,29	1,60
3-Methyl-2-pentene	0,64	0,68	0,00	0,37	0,16	0,93	1,11
2-Methyl-2-pentene	0,20	0,20	0,00	0,05	0,21	0,01	0,30
2-Methyl-1,3-pentadiene	0,16	0,07	0,00	0,13	0,09	0,05	0,12
2,4-Hexadiene	0,16	0,10	0,00	0,11	0,03	0,15	0,28
C1-C6	**12,91**	**19,59**	**0,18**	**6,72**	**3,54**	**10,53**	**13,51**
2,4-Dimethyl-1-pentene	0,38	0,34	0,02	0,26	0,03	0,12	0,49
2,4-Dimethyl-2-pentene	0,52	0,59	0,01	0,45	0,06	0,31	0,20
3-Methylhexane	0,08	0,20	0,00	0,06	0,39	0,18	0,09
2-Methyl-1-hexene	0,23	0,32	0,05	0,15	0,03	0,16	0,45
2-Methyl-2-hexene	1,12	1,03	0,01	0,57	0,77	3,04	1,99
3-Methyl-2-hexene	0,28	0,28	0,00	0,17	0,13	0,62	0,70
3,4-Dimethyl-2-pentene	0,23	0,01	0,02	0,16	0,10	0,47	0,45
4,4-Dimethyl-2-hexene	0,27	0,41	0,04	0,23	0,15	0,59	0,64
2,5-Dimethyl-2-hexene	0,61	0,09	0,01	0,35	0,25	1,17	1,23
4-Methylheptane	1,21	0,74	0,07	0,57	0,29	0,40	0,35
3-Octene	0,32	0,51	0,01	0,21	0,20	0,79	0,63
3,3-Dimethyl-1-hexene	0,42	0,72	0,04	0,41	0,11	0,32	0,46
C7-C8	**5,67**	**5,23**	**0,28**	**3,57**	**2,50**	**8,17**	**7,68**
3-Methyl-4-methyleneheptane	0,34	0,54	0,02	0,23	0,26	0,54	0,71
2,4-Dimethylheptane	0,17	0,17	0,02	0,07	0,10	0,07	0,16
2,2-Dimethyl-3-heptene	0,36	0,75	0,02	0,11	0,03	0,13	0,15
2,3-Dimethyl-2-heptene	0,83	1,92	0,01	0,03	0,11	0,09	0,08
2,4-Dimethyl-1-heptene	8,30	1,82	1,22	4,61	0,37	0,94	1,49
2,6-Dimethyl-3-heptene	1,18	0,19	0,02	3,00	0,10	0,54	0,46

2-Methyl-3-octene	0,20	0,46	0,00	0,22	0,37	1,03	0,70
2,3-Dimethyl-2-heptene	0,26	0,27	0,01	0,06	0,08	0,44	0,19
C9	**11,65**	**6,12**	**1,33**	**8,32**	**1,42**	**3,77**	**3,94**
2,4,6-Trimethyl-1-heptene	0,14	0,29	0,02	0,17	0,12	0,14	0,15
3-Decene	0,48	0,38	0,01	0,10	0,13	0,55	0,47
2-Methyl-3-nonene	0,21	0,39	0,05	0,29	0,24	0,73	0,70
2,6-Dimethyl-2-octene	0,35	0,50	0,00	0,11	0,05	0,33	0,42
2,4,6-Trimethyl-3-heptene	0,54	0,32	0,04	0,17	0,03	0,11	0,20
2,3,4-Trimethylhexane	0,55	0,03	0,28	0,48	0,01	0,02	0,23
5-Ethyl-2,4-dimethyl-2-heptene	0,74	0,48	0,02	0,56	0,11	0,39	0,43
2,6-Dimethylnonane	0,34	0,25	0,05	0,25	0,04	0,11	0,12
4-Methyldecane	0,35	0,21	0,06	0,24	0,05	0,10	0,17
2,3,7-Trimethyl-2-octene	0,88	0,20	0,06	0,82	0,05	0,11	0,46
4-Dodecene	0,21	0,33	0,00	0,17	0,05	0,21	0,47
3-Methyl-3-undecene	0,42	0,62	0,04	0,22	0,20	0,56	0,56
7-Methyl-4-undecene	0,37	0,24	0,09	0,29	0,14	0,44	0,33
8-Methyl-4-undecene	0,30	0,25	0,19	0,18	0,08	0,20	0,24
2,4-Dimethyl-2-decene	0,39	0,22	0,03	0,04	0,04	0,13	0,19
7-Methyl-1-undecene	0,39	0,34	0,22	0,56	0,07	0,12	0,46
2,4-Dimethyl-4-decene	0,19	0,29	0,05	0,18	0,10	0,26	0,34
5-Methyl-3-undecene	0,20	0,15	0,04	0,18	0,06	0,18	0,28
2,2-Dimethyl-3-decene	0,82	0,27	0,32	0,78	0,01	0,06	0,14
6,6,8-Trimethyl-1-nonene	0,79	0,12	0,17	0,59	0,01	0,06	0,00
4,5-Dimethyl-2-undecene	0,38	0,04	0,02	0,16	0,13	0,08	0,45
C10-C13	**9,04**	**5,93**	**1,76**	**6,54**	**1,71**	**4,88**	**6,83**
wt % heavy oil fraction	41,98	31,47	15,15	43,16	6,72	20,41	33,70
wt % not pyrolysed PP	2,10	0,25	75,96	12,97	73,52	15,02	1,20

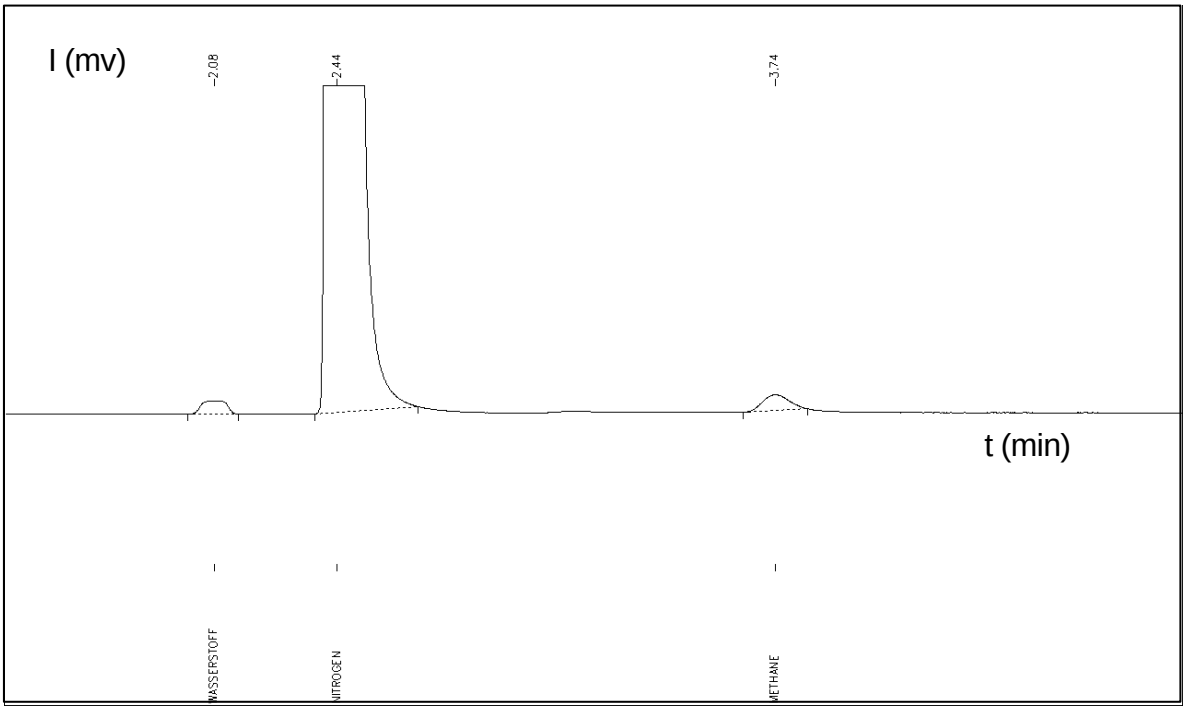


Figure A.1.- Permanent gases gas chromatograph

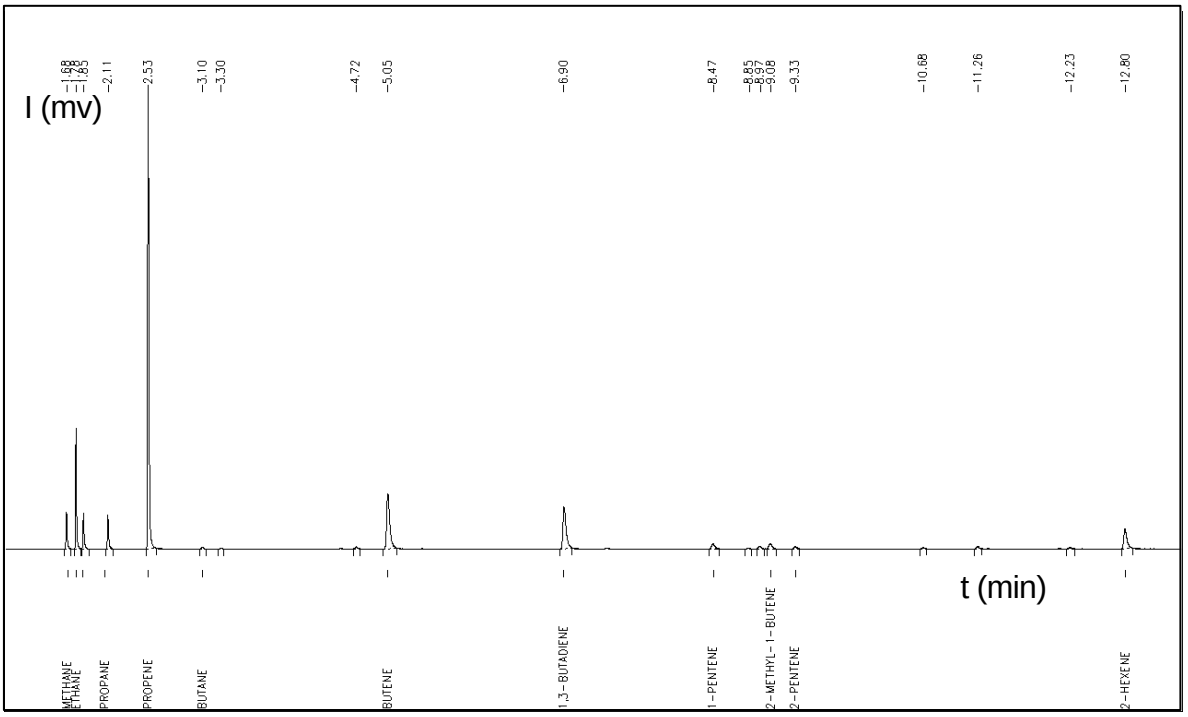


Figure A.2.- Hydrocarbon gases gas chromatograph

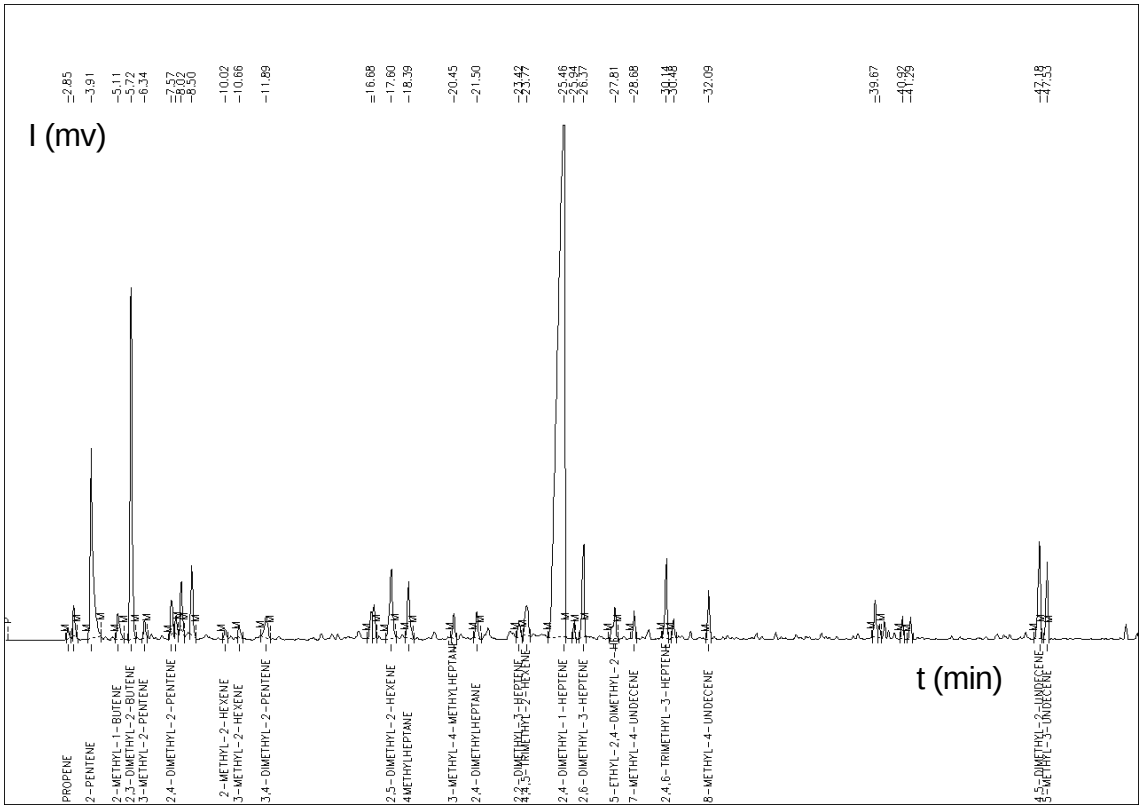


Figure A.3.- Oil fraction gas chromatograph

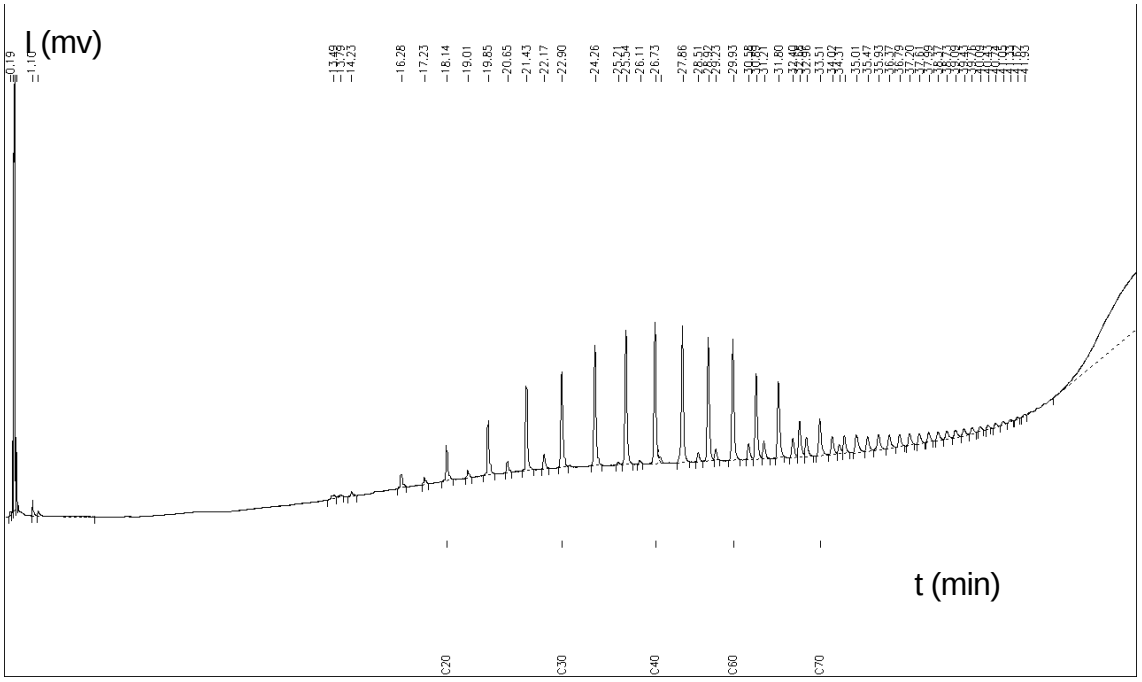


Figure A.4.- Wax fraction gas chromatograph

Table A.7.- Energy rates for a consume of 5000 kWh in Hamburg

Energy company	**Price (Ct /kWh)**	Rate per month (€)
Hamburg Energie Hanse	15,3	5,04
GGEW L Power GGEW	14,48	8,62
HanseArtStrom E.ON Hanse	14,83	7,76
Clever National entega	15,19	6,9
Hamburg Basic Vattenfall Hamburg	15,65	5,13
GGEW S Power GGEW	15,78	5,17
Gewerbe Lichtblick	15,95	5,95
GENO business ZT Geno Strom	15,25	8,95
PremiumExtraGewerbe Sw Schwäbisch Hall	15,34	8,62
5600er Paket FlexStrom GmbH Paket mit Vorauskasse[1]	16,24	6,5
Hamburg Newpower Vattenfall Hamburg	16,24	5,13
eprimoGewerbe eprimo	15,56	8,18
Moinpower Gewerbe 4 Strommixer	16,81	8,62
Hamburg Classic Vattenfall Hamburg	16,38	5,13
NaturPur light mitTB NaturPur	16,55	5,17
Hamburgs Best FlexStrom GmbH	16,9	5,3
eprimoPrimaKlimaG eprimo	15,91	8,18
AktivStrom I NaturStromHandel	16,59	6,72
Watt Ihr Spart 0,5 EWS Schönau	16,72	4,96
Hamburg Plus	HT: 16,25	7,33

Vattenfall Hamburg	NT: 12,43	
3600er Paket FlexStrom GmbH Paket mit Vorauskasse	17,08	6,5
Watt Premium Partner Watt GmbH	15,76	9,9
NaturPur light NaturPur	16,55	6,9
Hamburg Classic S Vattenfall Hamburg	HT: 16,51 NT: 12,42	7,33
GENO Strom business Geno Strom	16,25	8,7
Watt Ihr Spart 1,0 EWS Schönau	17,22	4,96
Regio+ EVH GmbH	15,65	12
Business Regio 4 Energie AG	16,09	11,49
Watt Ihr Spart 2,0 EWS Schönau	18,22	4,96
Naturstrom Silber Naturstrom	18,02	6,72
NaturPur prem. mitTB NaturPur	18,62	4,74
3600er Paket 3mon FlexStrom GmbH Paket mit Vorauskasse	18,88	7,5
NaturPur premium NaturPur	18,62	6,47
Gewerbe Kompakt Watt GmbH	15,94	17,9
Naturstrom Gold Gew. Naturstrom	18,75	6,72
5600er Paket 3mon FlexStrom GmbH Paket mit Vorauskasse	19,04	7,5
2400er Paket FlexStrom GmbH Paket mit Vorauskasse	19,8	6,5
NaturEnergie Silber NaturEnergie	19	8
NaturEnergie Gold NaturEnergie	21,5	8
Average	16,8144737	7,323

Declaration

I declare to have developed the results presented in this thesis myself, and with the help of no other than the cited references and resources.

This work has not been presented to any inspecting authority in the same or a similar form before.

Erklärung

Der Verfasser erklärt, die vorliegende Arbeit selbständig und ohne fremde Hilfe verfasst zu haben. Andere als die angegebenen Hilfsmittel und Quellen wurden nicht benutzt und die benutzten wörtlich oder inhaltlich entnommen Stellen sind als solche kenntlich gemacht.

Diese Arbeit hat in gleicher oder ähnlicher Form noch keiner Prüfungsbehörde vorgelegen.

Hamburg, den 13. Oktober 2006 _____

(Ignacio Javier Núñez Zorriqueta)

List of publications

Articles

Kaminsky, W.; Núñez Zorriqueta, I.J.; Catalytical and thermal pyrolysis of polyolefins, J. Anal. Appl. Pyrolysis, submitted.

Núñez Zorriqueta, I.J.; Kaminsky, W.; Degradation of polypropylene by Ziegler-Natta catalysts, Polymer degradation and stability, submitted.

Núñez Zorriqueta, I.J.; Kaminsky, W.; Pyrolysis of polyolefins by Ziegler-Natta catalysts, "Feedstock Recycling of Plastics" Selected papers presented at the 3th.international symposium on feedstock recycling of plastics, M.Müller-Hagedorn, H. Bockhorn (editors), 2005, 317-324.

Conference contributions

Talk: Kaminsky,W; Núñez Zorriqueta, I.J.; Catalytical and thermal pyrolysis of polyolefins, 17th International Symposium on Analytical and Applied Pyrolysis, 2006, Budapest.

Poster: Donner, M; Núñez Zorriqueta, I.J; Kaminsky W.; Pyrolysis-GC/MS: An Alternative Approach to Characterize Cyclo-Olefin-Copolymers (COC), 17th International Symposium on Analytical and Applied Pyrolysis, 2006, Budapest.

Poster: Núñez Zorriqueta, I.J; Donner, M.; Kaminsky, W.; Katalytische Pyrolyse von Polypropylen (PP), Hamburger Makromolekulares Symposium (HMS), 2005, Hamburg.

Poster: Núñez Zorriqueta, I.J; Donner, M.; Kaminsky, W.; Pyrolysis of polyolefins by Ziegler-Natta catalysts, 3rd International Symposium on Feedstock Recycling (ISFR), 2005, Karlsruhe.

Poster: Donner, M; Núñez Zorriqueta, I.J; Kaminsky W.; Chemical recycling and characterization of cycloolefin-copolymers (COC) by pyrolysis and catalytic pyrolysis of polypropylene (PP)), 16th International Symposium on Analytical and Applied Pyrolysis, 2004, Alicante.

Curriculum Vitae

Personal data

Name:	Ignacio Javier Núñez Zorriqueta
Birth date:	21.VII.1976
Birth place:	Bilbao, Spain
Marital status:	Single

Education

September 1982 – June 1990	Colegio A. de Urdaneta, Lujua (E.G.B), Spain
September 1990 – June 1993	Colegio A. de Urdaneta, Lujua (B.U.P.), Spain
September 1993 – June 1994	Instituto Lauaxeta (Munguia) (C.O.U.), Spain
June 1994	Selectividad

University studies

October 1994 – October 2001	Chemical engineering, University of the Basque country, Lejona, Spain.
October 2000 – October 2001	Master Thesis in the “New Material laboratory” , physical chemistry department, University of the Basque country, Lejona, Spain.
August 2002 – December 2002	Practical work in Interuniversity Microelectronic Center (IMEC), Leuven, Belgium.
May 2003 – August 2003	Researcher in Shell Global Solutions, Hamburg, Germany.
October 2003 – October 2006	Promotion in Prof. Kaminsky’s working group, Technical and macromolecular chemistry institute. University of Hamburg, Hamburg, Germany.