UNIVERSIDAD AUTONOMA DE NUEVO LEÓN

FACULTAD DE CIENCIAS QUÍMICAS

DIESEL REMOVAL FROM WATER BODIES USING A NEW RECYCLED SORBENT BASED ON LOW-DENSITY POLYETHYLENE DEGRADED WITH ZEOLITE

Por:

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Como requisito parcial para obtener el grado de:

MAESTRÍA EN CIENCIAS CON ORIENTACIÓN
EN QUÍMICA ANALÍTICA AMBIENTAL

SEPTIEMBRE 2021

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As partial requirement to obtain the Grade of
MASTER IN SCIENCE with orientation in
Environmental Analytical Chemistry

September, 2021

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Thesis Approbation

The members of the thesis commission approve the thesis made by the student Samantha Molina Flores, with enrollment 1553191 as an option to the degree of Master of Science with orientation in Environmental Analytical Chemistry.

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DEDICATION

Thanks to Universidad Autónoma de Nuevo León, to Facultad de Ciencias Químicas and Industrial Chemistry and Instrumental Analysis laboratories for the installations required during this project.

Thanks to Dr. María Guadalupe Sánchez Anguiano for the confidence given to be part of her work team.

Thanks to the tutorial committee for the revision of this project.

Thanks to Dr. Gloria Lourdes Dimas for the infinity recommendations all way long of the master’s degree.

Thanks to my mother, María de Jesús Flores Chávez, and my father, Abel Molina Rodríguez; their orientation, wisdom and strength allowed me to center my priorities on studies.

Thanks to my siblings, Abel Abraham and Jennifer, a long the time I have learned more from you than you from me.

Thanks to CONACYT for the scholarship given (888789).

SUMMARY

A new composite has been developed based on low density polyethylene (LDPE) and zeolite. This material was used to remove diesel present as pollutant in an aqueous system. In the process of synthesis and removal three effects were combined: the capacity of the zeolite to degrade polyethylene, the improve of thermodynamic interactions and the porosity of the composite. The material was synthetized in solid state through thermocatalytic degradation of LDPE in presence of zeolite (1:1) at 200 °C for 2,4 and 6 h. The materials obtained were characterized by DSC, TGA, SEC and XRD. The diesel removal took place in two systems: 1) Composite (S) + diesel (D) using 50 mg of the sorbent material and 200 mg of diesel and 2) S+D/Water (W) using 50 mg of sorbent, 200 mg of diesel and 800 mg of distilled water. The trials were shaken for 2 minutes and left to rest for 18 h. After, the diesel removal capacity was analyzed by TGA through the difference of weight loss at diesel evaporation temperatures (115-275 °C). All the prepared materials presented buoyancy and swelling, highlighting among them the material prepared at 2 h with a weight loss of 44 %.

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INTRODUCTION

In the last decades, the petroleum industry has increased abruptly due to the high demand of hydrocarbons all over the world. According to the U.S. Information Administration in 2018, the oil world production is around 100 million bbl/day [1]. Unfortunately, the industrial development through the production, transporting, distribution, storage and exploitation has increased discharge of petroleum products in water bodies [2]. Within these products found in oily water could be fats, lubricants, cutting liquids, heavy and light hydrocarbons [3]. The presence of petroleum products affects living organisms by physiological activity disorders, diseases caused by penetration of petroleum products and changes in the biological features of environment [4]. Even though different organisms around the world force the confinement of residual hydrocarbons, the reports of spills of petroleum products in water bodies continue increasing. Some examples of these spills are the Erika spill in France in 1999, the Prestige spill in Spain in 2002 and the Deepwater Horizon spill in the Gulf of Mexico in 2010 [5]. In addition, over the years the effects of oil spills can be seen not only in environmental damage, it also affects significantly the economy due to financial losses being estimated that the cost of cleanup for oil spills stand at 2 billion dollars per annum [6].

The plastic industry is heading one of the biggest industries since 1940, when synthetic polymers where introduced into industrial scale [7]. Among with hydrocarbons, the plastic waste has become a concern in environmental area. The big production of plastics has generated an alarming amount of waste in which the low-density polyethylene (LDPE) occupies the first position [8]. Polyethylene (PE) is the world's most used plastic, by 2018 the demand for it has been doubled since 1999 and by 2022 the global demand of PE is expected to be around 120 million metric tons [9] and it is estimated that each year one million sea birds, 100,000 marine mammals and countless fish are killed by plastic pollution [10]. These numbers highlight the need to develop a reuse and recycling system for plastic waste.

Different methods including landfill, incineration and plastic recycling have been employed for the disposal of plastic wastes. Nevertheless, disadvantages like high cost of producing electricity, close possibility for phased out landfilling and emission of toxic fumes from incineration are present [11-13].

In the case of hydrocarbons, some of the strategies used to remove oil spills include burning, booms and skimmers, chemical dispersants and sorbents. However, disadvantages are present. In the case of in situ burning, it can present adverse effects due to secondary products from the burning [14]. The use of booms and skimmers is not effective for large spills due to the cost that represents the expensive equipment [5,15,16]. Moreover, chemical dispersants involve the addition of chemicals materials to water bodies and can produce adverse effects [17,18]. A solution to the problems mentioned before could be the use of sorbents. There are three categories of sorbents: natural organic, natural inorganic and synthetic. In the market, the most commercial oil sorbents are composed of polyethylene [7,19-21] fitting in the category of synthetic sorbents. The natural inorganic sorbent category includes the zeolites. Zeolites are aluminosilicates capable of absorb 4 to 20 times their weight operating like a sponge collecting oil by capillary action [20,22-24]. Zeolites are not only used as sorbents. They also have catalytic properties that improve the efficiency of thermal degradation for waste plastics [8]. One of the most common zeolites is clinoptilolite. This kind of catalyst allows the penetration of the polyolefins into the reactive sites allowing the growth and end of products inside the pores [25].

Literature already suggested different oil polymer sorbents. Some are based on polyolefins, styrenic polymers or polyurethane foams or films capable of remove oil [8,21,26]. In the case of polyolefins different authors have demonstrated the capacity of PE for oil removal. Aboul-Gheit et al. reported PE in powder and sheets from plastic waste to evaluate oil-water separation efficiency but no retention values were measured [20]. Meanwhile, Chen & Chen [27] used LDPE to remove polycyclic aromatic hydrocarbons (PAHS) from liquid media with absorptions around 17.1-22.3 µg/g in 24 h. Using PE as removal agent is mainly focus on heavy fractions of hydrocarbons. The idea of this work is to remove the light fraction (diesel) dispersed in water. To attend this, degrading LDPE will produce short polyolefin chains with good affinity to diesel.

Singh & Sharma [25] review the general degradation conditions of polymers (photo-oxidative, ozone-induced, mechanochemical, biodegradation, thermal and catalytic). PE is sensitive to thermal degradation above 250 °C in air, leading to partially chain scission and producing olefinic fragments (hydrocarbons, waxes). The type and number of the degradation molecules is often not quantifiable and depend on many parameters as temperature, time, molar mass, branching and impurities. In the case of LDPE, it is known that most compounds obtained at average temperatures (250 – 350 °C) are average molar mass molecules whereas cracking degradation of PE [28] by zeolites above 400 °C give rise to only low molar mass molecules (less than 8 carbons). The degradation of PE into wax turn the material compatible with other waxes that are highly hydrophobic [29] as stated by Saleem et. at [8], that one of the ideal properties of oil sorbents is the good mutual solubility related with the similar structure of the sorbent and the oil. Since 1972, patents of oil spillage control are based on polyethylene waxes acting as water-repellent agents [30] where the presence of wax on sorbents improve the capability of the materials for oil sorption due to the hydrophobic properties conferred [31]. For example, J. Saleem et. al reported a degraded neat PE and gelled degraded PE as a sorbent with medium absorption properties for diesel removal [19].

As mentioned before, zeolites are the second piece in this project for the removal of diesel. Different authors reported Clinoptilolite as a zeolite capable of absorbing gasoline and diesel as mentioned by Mazeikiene et. al [22], Bandura et. al, found the sorption capacity of clinoptilolite for diesel around 0.36 g/g controlled by physical character over the external surface [24]. In addition, to functionalize a zeolite with hydrophobic surface treatments provides a material capable of adsorb oil, repel water and float on the surface of an oil-water mixture [23].

Advantages in combining natural inorganic and synthetic sorbents have been highlighted in 2015, where the removal of oil from water was enhanced modifying a polyurethane foam by integrating cloisite 20A nanoclay [32]. Also, Ajenifuja et. al removed crude oil from water using zeolite-modified polystyrene fibres obtaining an adsorption efficiency of 9.4 mg/g, higher than the raw materials [33].

The scientific contribution of this work is to combine three effects: capability of a zeolite to degrade PE at a controlled level (up to middle molar mass molecules e.g. wax), more favorable thermodynamic interactions between partially degraded LDPE (wax) and diesel, and finally porosity, thus an intrinsic absorption capacity of zeolites while some wax is inside the zeolite.

This strategy is aimed at developing a new sorbent based on a specific zeolite “clinoptilolite” and LDPE, to remove diesel. We provide insights of the new materials and their diesel uptake mechanism where zeolite plays the role of a catalyst and a capillary porous material. Our strategy is intended to be easy to handle, low cost, consuming as little as possible energy by choosing mild conditions for preparation of the sorbent material and a material able to use recycled materials. In addition, we investigate the fabrication, characterization of a new sorbent and sorbent capability of this new material compared to other sorbents.

2

THEORETICAL FRAMEWORK

2.1 Hydrocarbons

This project is focused in one of the biggest industrial sectors around the world: Hydrocarbons. Part of the human behavior is to control the nature to get benefits from it. Since the human learned to control fire to the development of machines to transport or cook aliments, hydrocarbons have become a need in our daily life. They are produced and processed in greatest amounts per day. Unfortunately, around history there have been some incidents that involved the spill of hydrocarbons into body waters. In this section we will go from the definition and classification of hydrocarbons to the effect of their presence in water until review different strategies for removing this pollutant from water.

2.1.1 Definition

Hydrocarbons are defined as organic chemical compounds mainly formed by atoms of carbon and hydrogen. They are highly dispersed in the nature. Most of them used today proceed from carbon, petroleum and natural gas. The petroleum is the biggest source and a mix of hydrocarbons [34] and is classified depending on the structure of the molecules or the properties given by the weight of the hydrocarbons that compose the mixture.

Table 1. Boiling Point of Aliphatic Hydrocarbons [35].

Alkane	BP (°C)
Pentane	36
Hexane	69
Heptane	98
Octane	125.5
Nonane	151
Decane	174
Undecane	196
Dodecane	216
Tetradecane	254
Pentadecane	271
Hexadecane	287
Heptadecane	303

All hydrocarbons are non-polar molecules with hydrophobic properties because of water repulsion [34]. Their density and boiling point increase depending on the number of carbon atoms, and so the molecular weight. The smallest molecules are found as gases in room temperature (C1-C4). By increasing the length and structural complexity of the molecule, it becomes liquid and more viscous (C5-C16). Hydrocarbons of high molecular weight are mainly solids in room temperature (>C16) [35]. In Table 1 the boiling point of aliphatic hydrocarbons from carbon 5 to carbon 17 are found.

2.1.2 Classification

Hydrocarbon molecules can be linear or cyclic and saturated or unsaturated (Figure 1) and could contain a low quantity of oxygen, sulfur and nitrogen [36].

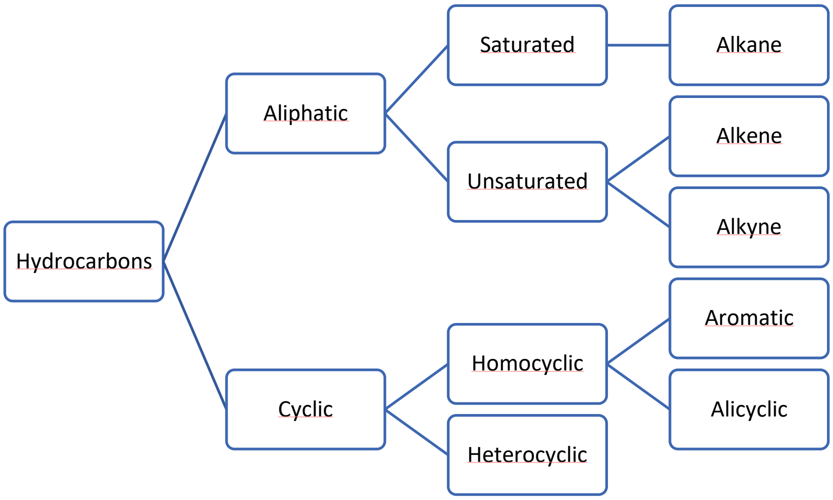


Figure 1. Classification of Hydrocarbons Based on Their Structure.

Hydrocarbons can also be classified depending on their weight given by the number of carbons in the molecules. Being divided as light, medium or heavy fractions, petroleum products are fractionated to produce mixtures for certain uses. The composition differs depending on the type of use, source and fraction. Light fractions contain a mix of hydrocarbons with molecules of 5 to 10 carbon atoms, medium fraction comprise molecules with 10 to 28 carbon atoms and the heavy fraction is composed by molecules with more than 28 carbon atoms. Normally the hydrocarbon products contain a mix of these fractions. In crude oil the three fractions are present. Paraffins and fuel oil are mainly composed of heavy fractions. Medium fractions are found in products as diesel, kerosene and turbine. Gasoline and naphtha gas are the classical mixtures of light fractions [37,38].

2.1.2.1 Diesel

As part of the medium hydrocarbon fraction classification with carbon numbers in C10 to C28 range, diesel presents a density of 0.84 kg/l at room temperature and a viscosity of 40 SSU at 37.8 °C (1.2-4.6 cST at 38 °C). It is composed of four kinds of carbons arranged in straight-chain branches, double or triple bonds and aromatic rings. The major composition is made of alkanes (83.7%) with an average of C14.2 and a 163.3 of aromatics. The 98% of diesel compounds are evaporated between 30 to 200 °C, but it can differ depending on the diesel compounds, as longer chains, heavier weight and higher boiling points [39].

2.1.3 Production of Hydrocarbons

Hydrocarbons became an essential energy resource and raw material for several industries with an increasing demand day to day [37]. As stated before, hundred million barrels of oil products are produced each day being the oil and gas sector as diesel essential to develop a strong economy [33]. Refineries are designed to maximize gasoline and diesel production as the primary transport fuel. Nowadays, diesel demand has increased worldwide, especially in Europe, due to the tax treatment, less severe vehicle emissions standards and the improvement of diesel vehicle performance [40]. In Mexico, at the end of the 20th century, Pemex Refinación, the most important refinery of the country processed more than 50 thousand of cubic meters of diesel per day [41].

Oil resources are the basis for global developments, unfortunately their processing represents a great hazard and pollution from spills and should not be left aside. Stated the need for development and industrialization of automotive industry, gasoline and diesel have become one of the major pollutants in environment [39].

2.1.4 Pollution of Hydrocarbons

Hydrocarbons are classified as priority recalcitrant pollutants [39]. Pollution can be present as punctual or systematics. Punctual pollutions come from fortuitous actions in body water with no common presence of hydrocarbons, while systematic pollution is commonly characteristic from water bodies contaminated by human activities realized over it. Frequently, pollution reaches storage systems, underground and superficial supplies. This kind of pollution produces a change in the organoleptic characteristics of the water where the ingestion represents a health risk; likewise, the ecosystem can suffer affectations due to negative impact for this contaminant under their different components [35].

Organic synthetic compounds such as petroleum products (PP) belong to a group of special pollutants of the hydrosphere where they migrate from soil contaminating water bodies. The pollution of water with PP commonly occurs from petroleum mining, production, oil refining processes, transportation (yearly average of 5 million tons), storage or when PP are washed away from contaminated lands [4,6]. Around the world, 5 million tons of PP are transported across the seas each year. Diesel has been found as an oily contaminant in polluted water [3]. The sea pollution by diesel can be produced during the daily operations of ships, by accident due to tank spills, hose or lines breakage or human mistakes in work, even by intentional way as waste dumps [42]. In Table 2 different disasters caused by PP spills are listed.

Table 2. Disasters in Water Bodies Caused by Petroleum Products [5].

Year	Disaster
1958	Regular petroleum leakages in the Niger Delta
1967	The wrecking of the Torrey Canyon
1969	The Santa Barbara channel plataform blowout
1970-1971	The Gulf of Mexico drilling rig incidents
1978	The grounding of supertanker Amoco Cadiz and the breakdown of the Piper Alpha Platform in North Sea
1989	The Exxon Valdez spill in Alaska
1991	The operation Desert Storm that released a huge amount of oil into the Arabian Gulf
1999	The Erika spill in France
2002	The Prestige spill in Spain
2010	The BP Deepwater Horizon spill in the Gulf of Mexico

2.1.4.1 Effects

As we can see in Table 2 waterbodies in worldwide level have passed through huge oil spill incidents. This represents financial losses, environmental devastation and attempts against living organisms. The presence of PP cause different adverse effects such as physiological disorders in living organisms and changes in environmental biological features, especially marine life is hardly affected by hydrocarbon spills, mainly diving birds and shell fishes [5].

The continuous exposition of hydrocarbons to skin cause irritation and dermatitis. Direct contact of lung tissue with liquid hydrocarbons by aspiration produces chemical pneumonitis, pulmonary edema and hemorrhage. The hydrocarbons with lowest molecular weight are the most toxic. After a spill of light and medium fraction hydrocarbons they can stay on water surface. They are toxic for plants and worms. Hydrocarbons with molecular weight higher than ethane are considered as general anesthetics and depressors of the central nervous system. Vapors of these hydrocarbons produce a light irritation of mucous incrementing this intensity with the number of carbons in the molecules [35]. The effect of hydrocarbons in marine organisms has different but still toxic behavior. There are fish larvae that are affected with low levels of 1 ppm meanwhile other fishes can hold concentrations that reach 1000 ppm [43]. Short term effects of marine environment caused by petroleum and derivates have been shown to be harmful depending of the quantity and type of pollutant, the place and the season [35].

This turned into the urgent need of preventing diesel among different types of PP from migrating in order to reduce its severe effects on hydrosphere and general environment.

2.1.4.2 Regulations

The World Health Organization (WHO) is the organism that proposes, regulates and make recommendations about international health matters. One of their goals is to guarantee to all people the access to safe drinking water. In order to achieve that goal, they publish International Standards for drinking water. In June of 2008 they stablished a background document for development of WHO Guidelines for Drinking water dedicated to the presence of PP. Guidelines for hydrocarbons in the medium fraction as diesel are stated by the WHO. In the case of aromatic fraction, maximum limits go up to 300-500 μg/l, and for aliphatic fractions a reference dose of 0.1 mg/kg [44].

Even though, in Mexico there is no regulation for the presence of diesel in water bodies, the effects of its presence in human health becomes a major problem, bringing the need of developing capable strategies of removing successfully these hydrocarbons from water bodies.

2.1.5 Solutions

Due to the health negative effects that represents the presence of hydrocarbons in water governments on world-wide level are becoming more strict on environmental chemical spills and the effectiveness management, which implies the necessity of developing low-cost materials in oil spill clean-up to avoid its migration and reduce adverse effects [39,45].

In order to remove oil spilled on water, different strategies have been used [33]. They are classified as chemical, biological and physical and mechanical methods [46]. Chemical methods include the use of detergents and dispersants. Their limitations include their expensive cost and toxic compounds that are dangerous to the aquatic flora and fauna [5]. Besides, they need a high requirement of energy to be mixed and they are not effective in thinner oils [47]. Biodegradation is a natural process to break up complex compounds by small organisms. Its application involves the artificial introduction of biological agents to speed up the natural process. It is often limited by the abiotic environmental factors as the lack of nutrients, low temperature and insufficient oxygen [48] which requires of a controlled system to improve the effectiveness. Physical techniques used are burning of floating oil on water, even though it has a 98% remove effectiveness, it attends negative effects on the ecosystem by the generation of large quantities of smoke that can result in oil rain [49,50], viscous residue that can damage the sea bed and its inhabitants and other safety concerns as the emission of toxic compounds [5].

Over the years, the looks are posed on mechanical techniques as booms, skimmers and sorbents. Booms and skimmer can result expensive by requiring many personnel and equipment [51], some other limitations are the attrition under harsh sea conditions, escape of oil under the boom, droplets and critical accumulation [52,53]. Sorbents materials have their best effectively when there are used at the end of the shoreline clean-ups or to recover oil from small areas. They are appropriated to recover less viscous oils in situations that are unsuitable for other techniques. Oil sorbents can be developed from organic, inorganic or synthetic compounds with the property of preferring oil than water [1]. They promise to be an effective tool thanks to their selectivity and low-cost.

2.1.5.1 Sorbents of Hydrocarbons

When a petroleum spill is detected, the first action to be carried out is containment. Floating booms are mainly used to contain the spill away from drinking water abstraction points. Methods used behind the containment boom are skimmers and sorbents [44]. As mentioned before, sorbents represent the best strategy to remove light oils as diesel. Sorbents act by adsorption or absorption. In adsorption the molecules in gas or aqueous phase are attracted and accumulated over the surface of the material [54] and absorption incorporates the oil inside the structure of the material [55].

In order to develop the ideal oil sorbent characteristics as fast and large sorption capacity, good selectivity, retention capacity, low-cost, hydrophobicity nature and insolubility in water should be present. Some of them are described below [5,55-57].

- Wetting properties

The oil should be capable of wetting the material by spreading over its surface in presence of water only if the surface tension of the oil is less than the critical surface tension of the material.

- Capillary action

It depends on the relative surface tension and the viscosity of the oil. As less viscous is the oil, it will penetrate faster.

- Cohesion/adhesion

Cohesion means that the material will attract itself avoiding spreading on a surface. And adhesion is the attraction of one material to another.

- Surface area

As bigger the surface area to volume ratio, including external and internal surface, the sorption rate will be better.

- Buoyancy

This is effective when the sorbent is used to remove floating oil, the material should stay afloat even when it is saturated with oil and water.

Different materials have been used as oil sorbents from water bodies categorized in three areas: natural organic, natural inorganic and synthetic sorbents [23,58,59]. Natural sorbents reported in literature include vegetable products such as sugar cane bagasse, vegetable filters, sawdust bed, zeolites, activated carbon, rice, straw or cotton but most of them present a low adsorption capacity [60-63]. They are economic but may also absorb water reducing their effectiveness [23]. Synthetic sorbents include rubber powder, expanded perlite, polymeric material, acetylated rice straw, inorganic clays and exfoliated graphite [64-70]. They can sorb up to 10 times their weight in oil [71]. Natural inorganic sorbents, also known as sinking sorbents, are highly dense mineral materials that include products such as zeolites, graphite, silica or natural clays [5]. They may be limited for their tendency of releasing some of the oil already sorbed due to their low retention capacity [72], but this feature can be improved with the modification of the structure as we will see forward.

2.2 Polymers

Nowadays there is no corner around the world without the presence of polymers. In this chapter we will see their classification and different uses, especially for plastics, which high demand has turned into environmental problems. As well, solutions in this area will be reviewed.

2.2.1 Definition

The polymers are the principal organic materials. They are macromolecules of high molecular weight constituted by smaller structural units disposed in tandem called monomers [34,73]. They are organic molecules of big interest due to their physical properties [74]. Their production is called polymerization process which starts from reactive low-mass compounds resulting in macromolecules united by a C-C backbone chain [75].

2.2.2 Classification

They are classified as natural or artificial depending on their origin. Natural polymers come from plants or animals, example: cellulose, wool or asbestos. Artificial polymers are produced from petrochemical sources or silicones. They also can be classified in order to the size of the molecule, structure, physic state, chemical composition, final use or behavior [73].

- Structure

Polymers are divided as a group of separable molecules or as a macroscopic web, as lineal or branched, and as a succession of aleatory units or preferent order.

- Physical state

The molecules of a polymer can be partially crystalline or completely disarranged. In a disarranged state, the polymers are fragile and have viscosity similar to liquids and elasticity similar to a rubber solid. These characteristics depend on the temperature, molecular weight and chemical structure.

- Chemical composition

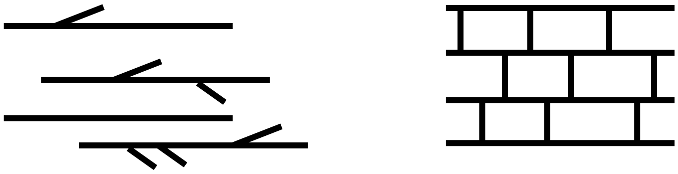
The chemical groups (ethylene, ether, ester, hydroxyl, etc.) or the synthesis (chain propagation, ring opening) give specific properties to the polymers.

- Final use

Depending on the properties given to the material they are often classified as fibers, adhesives or rubbers based on their applications.

- Behavior

The polymers behave differently based on the temperature of exposition. They are divided as thermoplastics, elastomers and thermostable polymers. Thermoplastics are soft materials that flow when pressure and heat are applied, capables of being remolded several times reaching and viscous-liquid state, and when they are re-cooled they become solid and capable of absorb mechanical strength. In the thermoplastic group polyethylene, polypropylene, 1-polybutene, polystyrene and polychloride of vinyl (PVC) are found [76]. In the other hand, when thermostable or elastomer polymers are heated, they react irreversibly and no pressure or heat make them soft or flow. Elastomers present an elastic and rubbery consistency and thermostables present a hard and rigid consistency. The difference between thermoplastics and thermostable polymers are seen in Figure 2.



Thermoplastic Thermostable

Figure 2. Representation of the Molecular Chains of Thermoplastics and Thermostable Polymers.

Polyethylene is formed by atoms of carbon and hydrogen linked in ~(CH_2-CH_2)~ units in all the chain (Figure 3). They are hydrocarbons of high molecular weight presented as a semi-crystalline material with a symmetric molecular structure and it is the most chemical simple polymer [77] presenting chemical properties of an alkane of high molecular weight [78].

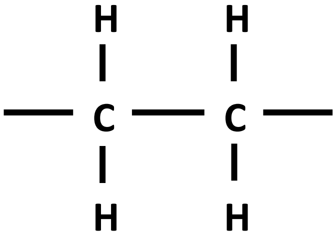


Figure 3. Monomer Group of Polyethylene Chains.

There are different types of polyethylene depending on the branching grade that confers different physical characteristics. The division goes as: high density polyethylene (HDPE) and low-density polyethylene (LDPE). HDPE is constituted by macromolecules lowly branched, big crystallinity and high resistance, meanwhile LDPE is formed by highly branched molecules and with a lowest crystallinity and resistance compared to HDPE [76].

2.2.2.1 Low-density Polyethylene

As mentioned before, LDPE presents a high branching grade, the melting point is 105-110 °C, its apparent density is 0.86-0.92 g/ml, the resistance and hardness is very low and is capable of a high elongation [76].

2.2.3 Production of Polymers

Polymers are characterized by their easy modelling, properties and low cost of production [79]. Their extensive consume comes from packaging, household, automobile, aerospace and electronic industry sectors [80] used as structural elements, textile covering and ornamental artefacts in form of fibers, films, adhesives or foams replacing materials such as metals [73].

The plastic consumption continues increasing due to the physicochemical properties and the cost-benefit relation the allow us to substitute the use of paper, glass and metals. In 2012, the world plastic demand reached 280 million tons [81] and it is expected that in 2020 this number will increase to 380 million tons [82]. Around a 50 % of plastic demand belongs to the group of the polyolefins. LDPE represents the majority part of this group. Its versatility and large applications including the production of wrapping papers and plastic bags have increased their production in the last years [28,79]. In 2012, the LDPE production was reported to be around 21 million tonnes with an excepted wroth of 700,000 tonnes per year [83].

It is well known that plastics have turned into an economical product that improves the lifestyle, but the overrated production became into an environmental problem as we will see in the next section.

2.2.4 Pollution of Polymers

Around the world the production of municipal plastic waste is becoming a serious problem. The high stability and resistance of plastics with their extended use turned their disposal in landfills an environmental problem [28]. The principal plastic sectors that contributes to this problem are containers and packaging producing a big amount of waste derived from their short service life [79]. In the EE. UU by 2012, 251 million tons of waste were produced and a 12.7% were plastics. In this percentage, polyethylene occupied the first position [79,84].

2.2.4.1 Effects

Polyethylene waste is affecting marine and terrestrial environments [85] representing the major threat in urban areas for public hygiene. When it is stocked in dumping yards it becomes the breeding ground for mosquitoes and flies that can carry dangerous diseases mainly in rainy seasons [86]. In the aquatic environment platics occasionate severous effects [87]. Oceans and coastal areas are full of polyethylene bags that decrease the marine fauna population when fishes and birds ingest plastic debris by mistake [88].

Besides environmental affectations, the diminution in waste dumps turned into elevated cost for disposing solid waste [7]. The contamination levels and the cost linked drive the reuse and recycling of polyethylene.

2.2.4.2 Regulations

Divers politics have been redacted around the world to prevent and minimize the generation of polymer waste. As an example, some countries have applied taxes on dumps and in the incineration of waste. Also, the responsibility of waste products is now delegated to productors [79,89,90].

2.2.5 Solutions

While avoiding the generation of plastic waste is not possible to be carried out yet, new strategies to reuse and recycle waste are investigated [79].

2.2.5.1 Plastic Recycling

In polymers, degradation is defined as a property change caused by reactions that break links. In the case of polymers, degradation can affect physically, chemically or mechanically. The natural degradation mechanisms involve slow kinetics keeping a time of 500 years to degrade plastics [25]. Heat, radiation, chemical substances and mechanical energy can reduce considerably the time to produce this degradation [73].

- Thermal degradation

Polymers can be molten or decomposed at temperatures between 400 and 800 °C. They are broken in small fragments obtaining hydrocarbons with a wide distribution of carbons due to covalent unions that present a limited resistance [79]. The products obtained usually follow a range of carbon number between C6-C25 [91]. Onwudili et al. [92] realized the thermal degradation of LDPE where waxes were produced at 450 °C. Different authors have obtained similar results of the degradation of PE were waxes and liquids as alkenes and linear alkanes are produced between 450 and 650 °C [93,94]. Manos et al., demonstrated that the degradation of PE starts at 430 °C and reaches a maximum degradation velocity at 500 °C [95]. Due to the high temperature required to carried out a thermal degradation, the use of catalyzers have been employed to reduce the energy and time of degradation [79].

- Catalytic degradation

Among the advantages of using catalyzers to degrade PE is the control on the distribution of products obtained and the selectivity in the oil range [79]. The use of zeolites as catalyst in polymer degradation has been interesting for their superior catalytic properties [96,97]. Tthese examples will be further described.

Thanks to the thermoplastic characteristics that presents the LDPE, it can be recycled [76]. It has been demonstrated that products from the catalytic cracking of LDPE waste are obtained with similar characteristics to fossil fuels and can be used as an environmental solution to remove medium and light hydrocarbons such as diesel [98]. This point will be discussed in the next section.

2.2.6 LDPE as Sorbent

Polyethylene (PE) is one the most used materials to sorb oil due to its low cost [19]. It has been used to remove different class of hydrocarbons as pure material or combined with other polymers. As example, hybrid fibers of PE and PP (1:1) have been used to remove diesel in the Siberian region [4] in a dynamic and static regime. It was shown that in a static regime the sorption capacity for diesel was 17.9 g/g. Also, the efficiency of the removal of benzene and toluene in water by a physical mix of LDPE and PS (1:1) was evaluated by Belandria [89] but this mix did not present an improvement in hydrocarbon removal compared to the polymers used by separated.

Several oil sorbents have been synthesized by Saleem et al. from PE. These films presented a high sorption capacity and a fast uptake kinetic [19,26,99,100]. PE as a synthetic sorbent has been reported to be best suited to absorb lighter viscosity oils. Aboul et al. [20], applied a PE in the form of powder and sheets for sorbing two kinds of crude oil (one heavier than the other) in sea and fresh water. No measurable difference was found on data by using the fresh or sea water which indicates that salinity is ineffective, and the oil sorption is directly correlated to the polymer and has no interference from the aqueous phase. Oil uptake capacity was not reported because their aim was only the oil-water separation efficiency. Also, they report a higher efficiency of sorption for the higher oil than for the lighter.

Sachets of polyethylene waste were used by Edoga et al. [101] as adsorbents to remove oil spilled on water as a low-cost adsorbent. The sachets were collected, preheated in hot boiled water with detergent for ten minutes, washed and dried to be later pulverized with a hand grinder obtaining particles of 2 mm to adsorb crude oil in different time intervals obtaining a 100% of cleaning within a time of 3 h being an safe, rapid and inexpensive manner to successfully remove crude oil.

In 2015 Chen & Chen [27] reported the use of LDPE to in the removal of polycyclic aromatic hydrocarbons (PAHs) from different liquid models. Five carcinogenic PAHs were employed to monitor the sorption process. In the first 24 h more than 50 % of adsorption was reported. The water-oil system got the highest PAHs removal by LDPE and the residual PAHs had to be decreased with UV radiation.

However, PE alone possess a low medium and light hydrocarbon fraction sorption capacity. A technique that has improve the capacity of PE to sorb light oils is to subject the PE to low doses of gamma irradiation [20] which produces a low degree of cross-linked structures which facilitates the penetration and sorption of oil into the polymer. New strategies are in the aim of science to find the way to improve this capacity such as the partial degradation of PE in order to improve the thermodynamic interactions with medium and light fractions. In this work the removal of diesel is proposed through a new composite based on degraded polyethylene with zeolite.

2.3 Zeolites

Zeolites are minerals widely spread on nature. The diameter of pore and topology of each zeolite make them capable of diverse applications such as adsorption and separation of compounds, catalysis, microelectronic and medical application [102]. In this work zeolites will be used as modelling cavities for the thermal degradation of LDPE and as a part of a new composite for diesel removal. In this chapter we will review the characteristic and applications of zeolites, specially clinoptilolite in the field.

2.3.1 Definition

Zeolites are three-dimensional solid crystalline aluminosilicates composed of silica (SiO_2) and alumina (Al_2O_3) in different proportions and may also contain metallic oxides. The tetrahedral building block of zeolites linked with oxygens produce an organized network formed by pores with diameters < 20nm with uniform dimensions [102,103].

2.3.2 Classification

Zeolites can be classified by the number of oxygen atoms that form the rings or pores. Being classified as zeolites of extralarge por ($\theta > 9$ Å), large pore (6 Å $< \theta < 9$ Å), medium pore (5 Å $< \theta < 6$ Å) and small pore (3 Å$< \theta < 5$ Å) depending on the access to the interior of the structure through rings of 18, 12, 10 or 8 oxygen atoms [104].

2.3.2.1 Clinoptilolite

The chemical composition of clinoptilolite is [$Na_{1.84}K_{1.76}Mg_{0.2}Ca_{1.24}(H2O)_{21.36}$] [$Si_{29.84}Al_{6.16}O_{72}$] and it is recognized by the distances d_{hkl} = 8.95; 794; 3.96; 3.90 Ǻ. In their natural form, clinoptilolite forms crystalline thin plates with hexagonal shape. The size of each unit is about 10 μm. The specific surface area is 18.3 m^2/g with an average diameter of pore of 10 nm [24].

2.3.3 Properties

Zeolites have different properties and uses given by a variety of factors such as the crystallinity of the structure, uniform pore size and the presence of strongly acidic hydroxyl groups [103]. Their used is report in medicine, industry, agriculture, water purification, sorption, etcetera [105], and mainly known by their catalytic activities.

2.3.3.1 Catalytic Activity

Zeolites have been reported to be successful to convert polyolefins into liquid fuels giving lighter fractions compared to thermal cracking [7]. They are widely used due to the acid centers presented in the catalyzer that allows the breakage of the C-C bond through reactions of oxygen transportation [106]. The catalytic degradation of plastics in presence of zeolite is described in the following steps:

a) Initiation: It begins on the zeolite surface. Macromolecules of the polymer react with the active sites on the external surface of the catalyzer [107]. Two kind of reaction can take place: the abstraction of a hydride of the polymer by action of the acid Lewis sites, or the addition of a proton to the C-C bonds by action of the acid Brönsted sites [108]. These reactions take place preferentially on defect sites of the polymer chain [109].

b) Propagation: The products obtained from the initial rupture reduce the length of the polymer through successive attacks by the acid sites of the catalyzer, producing an oligomer or shorter size (C30-C80). These fragments are incrusted in the internal structure of the zeolite and continue reacting with the acid sites [95,110] producing lightest chains (C10-C25).

Clinoptilolite has been used for the thermo catalytical degradation of LDPE. Tomaszewka et al., [111] being clinoptilolite the zeolite with the lowest degradation temperature required compared to four different types of montmorillonite. The products obtained were distributed in carbon fraction of C8 to C26.

2.3.3.2 Sorbent Properties

As mentioned before, zeolites are part of mineral compounds used as oil sorbents. They are not toxic for human beings turning them into a good material to remove hydrocarbons from water bodies. The hydrophilic character and pore size of each zeolite allows certain molecules of a size range to diffuse into the structure acting as sorbents [103,112].

Clinoptilolite as PP sorbent was reported by Sirotkina & Novoselova [4]. The minerals were obtained from natural deposits and were tested for the extraction of petroleum from water. A 100 % of purification of emulsified oil water was reached. The authors conclude mechanisms of adsorption and absorption of the pollutant into the zeolite particles.

A second study of clinoptilolite properties to remove diesel was reported by Franus et al [24]. It resulted in removal capacity of 0.25 g/g. This could represent a small sorption capacity compared to commercial materials due to the narrow pores. In order to solve this problems composites that combine polymers and zeolites are proposed.

2.4 Composites Based on Polymeric Compounds and Zeolites

Sorption materials based on polymers and zeolites, known as mix matrix membranes (MMM), are commonly used in the chemical and petrochemical industry. MMM combine separation properties, selectivity and intramolecular size of zeolites with the processability and low cost of polymer membranes [113]. Membranes are formed in a solid-solid system with an inorganic phase (zeolite) dispersed on the polymer matrix [32,33,112].

Nikkhah et al. [32], modified polyurethane foam (PUF) structures by integrating 20A nanoclay into it in order to enhance the removal of oil contaminants from water compared to the polyurethane alone. The sorption capacity was improved up to 16% and oil removal efficiency up to 56% in water-oil system. They confirm that the presence of the nanoclay on the PUF enhance the foam strength and open its cells.

Polystyrene-zeolite fibres were fabricated using electrospinning technique to improve the crude oil-water separation by adsorption [33]. This new fiber showed the highest adsorption efficiency (9.4 mg/g) compared to PS foams and fibres.

These previous reported investigations open a scientific window to develop materials based on polymeric waste degraded and integrated in zeolite to produce a new composite sorbent capable of remove diesel from water with a high selectivity.

2.5 Characterization Techniques

In order to understand the physical and chemical behavior of a new material its characterization is required. Most used techniques to characterize polymer and zeolite materials involve infrared spectroscopy with Fourier transformation, differential scanning calorimetry, thermogravimetrical analysis and size exclusion chromatography. These techniques will be described in the next sections.

2.5.1 Fourier-transformed Infrared Spectroscopy

Infrared spectroscopy is a versatile technique where spectra are easily obtained from liquid, solid or gaseous samples [114]. The molecular spectroscopy is based on the interaction between electromagnetic radiation and molecules. Depending on the spectrum region the interaction can present different natures: excitation, vibration and rotation [115]. When the molecule absorbs infrared radiation the energy state is changed, only vibrational energy states are considered in FT-IR due to the energy required [116]. This technique is the starting point to understand the structural characteristics of a new material based on its parent materials.

2.5.2 Differential Scanning Calorimetry

DSC technique is used in polymers to investigate their properties on a certain heating range at a specific rate to obtain mainly the melting and crystallization as first order phase transitions of the examined samples. This is obtained as a transition where the heat capacity is in function of time and temperature has a discontinuity as a shape of a peak. With the area under the peak the energy emitted or absorbed is directly proportionated obtained in the state changes of the sample. The highest point in the peak is the temperature or time where most of the molecules that compound the sample are represented as a melting, crystallization or polymerization reaction takes place [114].

2.5.3 Termogravimetrical Analysis

It is a weight loss measure technique were very small quantities of samples are required. [117]. TGA is described as a potential method to follow the oxidative thermal or catalytic degradation of polymers [107,118]. In a TGA instrument samples are submitted to constant heating rate from room temperature up to 600 °C inside a furnace under nitrogen or air flow [25]. It also provides information about catalytic activity of zeolites on the degradation of PE [77]. TGA can be employed in two methods: isothermal and non-sithermal [119,120]. Non-isothermal methods consume less time compared to isothermal methods [120]. In isothermal methods, the temperature remains constatnt and is recommended when intermediates from decomposition/pyrolysis of waste plastic want to be observed [121].

2.5.4 Size Exclusion Chromatography

The principal objective of this technique is to separate molecules to obtain information about molecular weight and distribution of polymers [122]. This technique provides a separation of a material based on its size, allowing the smaller analytes in solution to diffuse into the media pores while larger analytes are swept in the column by the solvent. To obtain valid data, analytes should not be stick on the surface of the column particles avoiding an interaction effect that will produce wrong retention times not based on the size. The selection of the surface interaction is the most important step in this technique [123]. Nowadays, the technique is fast and allows elevated pressures using new column materials with specific pores distributions ant mechanical resistance [124].

2.5.5 X-ray Diffraction

This technique is based on the diffraction phenomenon where the x-ray source, the sample and the detector are geometrically arranged in order to hit the sample with an x-ray beam. Once the beam is diffracted, it is redirected to the detector recording the intensity of x-rays. In this way, the pulse generates a diffraction pattern [125]. The diffraction patterns are used to identify the crystalline structure of solids. In the case of zeolites, they have a specific special crystalline disposition that characterizes each type [126], allowing the phase identification of an unknown mineral material is possible thanks to XRD [127]. It is characteristically use in zeolite identification using 2θ mode from 5 to 70° [24,28,127,128].

2.6 Diesel Quantification

In order to quantify the sorption capacity of PP removal by sorbents different strategies have been applied, including: TGA analysis [23,39], gravimetrical measurement [24,32,101,129,130], LED, fluorescence or UV spectrophotometers [20,131,132] and chromatography techniques [27,35,89,133]. Most chromatography techniques are based on physical principles where the compounds from a sample migrate at different velocities on a stationary phase inflected by a mobile phase [134]. Through chromatography separation is possible to identify and quantify the compounds in a sample.

2.6.1 Gas Chromatography

This is the most used technique for diesel measurements, it is carried out in a mobile gaseous phase and a liquid stationary phase supported to a solid. The process begins with the injection of a gaseous sample on the column head. The compounds differentially flow on the column with the help of an inert carrier gas, normally nitrogen [35]. The detector is placed at the end of the column, being FID the most used for hydrocarbon analysis because of its linear response over a large concentration range [27].

2.7 Adsorption Capacity

The adsorption capacity is characterized by the quantity of material that can be adsorbed or absorbed by an immobilized form. To calculate this, differences are quantified between initial pollutant concentration (diesel) and final concentration in the aqueous phase using the following equation:

$$q = \left(C_i - C_f\right) \frac{V}{m}$$

Where C_i is the initial concentration of diesel in solution (mg L^{-1}), C_f is the diesel concentration measured in an instant of the process (mg L^{-1}), V is the volume of the solution (L) and m the dose of sorbent applied (g); finding q, expressed as the mass of diesel sorbed per unit of sorbent (mg g^{-1}) in an instant of the process. In base on the duration of the process the equilibrium corresponded to the concentration is obtained, q_{qe}.

3

HYPOTHESIS AND OBJECTIVES

3.1 Hypothesis

The material formed from the low-density polyethylene degraded with the presence of zeolite removes diesel of water bodies to a greater extent than undegraded PE.

3.2 Objectives

3.2.1 General Purpose

Remove diesel of water bodies using the degradation product of low-density polyethylene with the presence of zeolite.

3.2.2 Specific Objectives

Degrade thermally and partially LDPE in the presence of zeolite.

Characterize the degradation products by Fourier transform infrared spectroscopy (FT-IR), size-exclusion chromatography (SEC), differential scanning calorimetry (DSC), Thermogravimetric Analysis (TGA) and X-Ray Diffraction (XRD).

Establish an analytical technique to determine diesel present in water using Thermogravimetric Analysis and Gas Chromatography.

4

METHODOLOGY

4.1 Materials

Low density polyethylene (Sigma Aldrich, USA)

Zeolite (Industrial corporation, Mexico)

Acetone (Sigma Aldrich, USA)

Toluene (Sigma Aldrich, USA)

Trichlorobenzene (Sigma Aldrich, USA)

Diesel (Local market, Mexico)

4.2 Methods

4.2.1 Preparation of Materials

The pellets of LDPE were triturated in a Retsch Ultra Centrifugal Mill ZM 200 to obtain a white powder of around 40 µm. 10 g of clinoptilolite (20 µm) were activated by heating in a Thermo Scientific M110 muffle furnace in air at 200 °C for 2 hours to remove adsorbed water. This sample is labeled as HZ (heated zeolite) while crude zeolite is named ZEO.

4.2.2 Thermal Degradation of Low-density Polyethylene

In order to evaluate the thermal degradation of the LDPE, a sample of this material was put in the muffle furnace and heated at 200 °C for 2 hours. This product was labeled as LDPEdeg**.**

4.2.3 Catalytic Degradation of Low-density Polyethylene

For the catalytic degradation a blend with a weight ratio of HZ and LDPE 1:1 was prepared by solid state mixing by adding acetone as dispersant in a mortar and it was mixed until the acetone was totally evaporated. This product was put in the muffle at 200 °C for 2 hours. The same procedure as described above was repeated increasing the time of degradation to 4 and 6 hours. These final products were labeled as DPZ-*n,* where *DPZ* is degraded polyethylene with zeolite and *n* the hours of degradation.

4.2.4 Characterization of Materials

4.2.4.1 Identification of Zeolite by XRD

To confirm the type of zeolite used in this project the zeolite and HZ were submitted to XRD with a scan range of 5 to 85 degrees, a speed of 5 °/min and an axis of 2 theta in a Rigaku MiniFlexII diffractometer. The results were compared to diffractograms in literature [24]. The LDPE, products DPZ-0, 2, 4, 6 and ZAE-2, 4, 6 were also evaluated.

4.2.4.2 Wax Extraction

After the degradation period, 2 g of the products DPZ-2, DPZ-4 and DPZ-6 were stirred and left in TCB for 2 hours at 130 °C and then separated in two phases through a hot filtration with TCB in a 113 Whatman paper. The solid phase was labeled as ZAE-*n* where *ZAE* is zeolite after hot extraction and *n* the hours of degradation. The liquid phase, in which degraded polyethylene was tentatively extracted from DPZ, was left at 130 °C until TCB was totally evaporated. Each product was labeled as WAX-*n* where *n* is the hours of degradation.

4.2.4.3 Characterization by FT-IR

The characterization of LDPE, zeolite and DPZ-4, was carried out in an infrared spectrophotometer with Fourier transform in the range of 500 to 4000 cm^{-1}.

4.2.4.4 Analysis of Thermal Transitions by DSC

The thermal transitions of LDPE, LDPEdeg, ZEO, HZ, DPZ-0, 2, 4, 6 and ZAE-2, 4, 6 were obtained using a TA instruments Q100 RCS temperature ramp from 20 to 250 °C with an increasing ramp of 10 °C/min. Using around 5.5 mg for the raw materials and 11 mg for DPZs and ZAEs.

4.2.4.5 Characterization by TGA

The thermogravimetric analysis was carried out in a TA instruments Q500 for LDPE, LDPEdeg, ZEO, HZ and DPZ-0, 2, 4, 6 obtained in air and nitrogen atmosphere separately, using 25 mg samples of each with a temperature ramp from 25 to 700 °C at 10 °C/min and an isothermal plateau at 200 °C for 6 h in the case of DPZ-0.

4.2.4.6 Determination of Molecular Weight Distribution by SEC

LDPE, WAX-2, WAX-4 and WAX-6 were solubilized separately in TCB heating at 130 °C during 10 min obtaining a final concentration of 0.2 % and analyzed in a PL-GPC 50 Plus (Agilent Technologies) with IR and viscometer detector. Molar masses are calculated with IR traces.

4.2.5 Sorbent Selection by TGA Analysis

Based on the proposal of Sakthivel et al. [23], diesel sorption capacities of LDPE, zeolite, DPZ-0, 2, 4, 6 and ZAE-2, 4, 6 were measured by TGA. First, in a test tube (100 mm, 8 mm) 50 mg of each sorbent were put in contact with 200 mg of diesel, stirred for 2 min and left for 18 h. Then, the samples were poured out on a 113 Whatman paper for 5 min to remove the excess of diesel. From each sample, 25 mg were analyzed in the TGA with a temperature ramp from 25 to 500 °C at 20 °C/min. This system was named as S+D. In order to evaluate the selectivity of the sorbents for diesel in presence of water, 50 mg of each sorbent was put in contact with 200 mg of diesel and 800 mg of distilled water for 18 h and the same procedure was carried out. This system was named as S+D/W. The diesel sorption capacity was quantified by the weight loss between 100 and ~280 °C, which is the temperature when the degradation of LDPE, present as a wax, begins. *S* stands for sorbent (whatever type), *D*: diesel or *W*: water.

4.2.6 Diesel Removal Essays

To quantify diesel sorption capacity of the selected sorbent gas chromatography is applied. The quantification essays are carried out in a Perkin Elmer Clarus 500 GC-FID with a temperature ramp as indicated in Table 3 using as stationary phase poly (dimethyl siloxane), and 16 mL/min of nitrogen as carrier gas. The injection volume was 10 μL with injector and detector temperatures at 250 °C. The detector flow was stablished as 400 mL/min for air and 40 mL/min for hydrogen. The total run lasted 40.83 min.

Table 3. Temperature Ramp Used in GC Analysis.

Temperature ramp		
Ramp rate (°C min^{-1})	Setpoint (°C)	Hold time (min)
	40	0
13.00	110	0
4	140	0
8.5	250	15

4.2.6.1 Curve of Calibration

Five different 10 g standards from 100 to 1019 mg/g concentrations were prepared by triplicated using CH_2Cl_2 as solvent and 10 μL of THF as internal standard. The integration of peaks areas was obtained with the TotalChrome Navigator software. The sum of the integrated area under the chromatogram peaks that belong to diesel compounds (AD) was divided by the integrated peak area of the THF (ATHF) as the internal method establish. The relation between AD/ATH and concentration was found through a linear regression obtaining the equation the correlates these values.

4.2.6.2 Semi-validation of Gas Chromatography

In order of knowing that the sorption results of the selected material are trustable a semi-validation of the technique was carried out evaluating liquid-liquid extraction recovery, minimum limits of detection and quantification and accuracy of the method.

- LLE recovery

Diesel removal essays were carried out in water systems. Given that diesel is not soluble in water, liquid-liquid extractions were necessary to quantify the real concentration of diesel. The recovery percentage of the extractions were evaluated by preparing 10 g triplicates of 490 and 1000 mg/g diesel in water concentrations. The LLE was carried out using 10 g of CH_2Cl_2 as extractant solvent and 8.0 μL of THF previous the injection of the feeding in the GC. The recovery percentage was obtained from the relation of initial and final concentrations.

-LOD and LOQ

The limits to detect and quantify the minimum concentration of diesel present in the samples were obtained through the formula:

$$LODx = S_b + (3 * SD) \qquad LOQx = S_b + (10 * SD)$$

Where S_b is the minimum signal obtain from the standard with the lowest concentration (100 mg/g), and *SD* is the standard deviation of three triplicates of that standard. The LOD_y and LOQ_y are obtained by applying the linear equation from the calibration curve.

-Relative Standard Deviation (RSD)

It is obtained with the formula

$$RSD = \frac{S * 100}{\bar{x}}$$

Where S is the Standard deviation of the concentrations calculated from the repetition of the lowest point in the calibration curve and $\bar{x}$ is the average of these repetitions.

5

RESULTS AND DISCUSSION

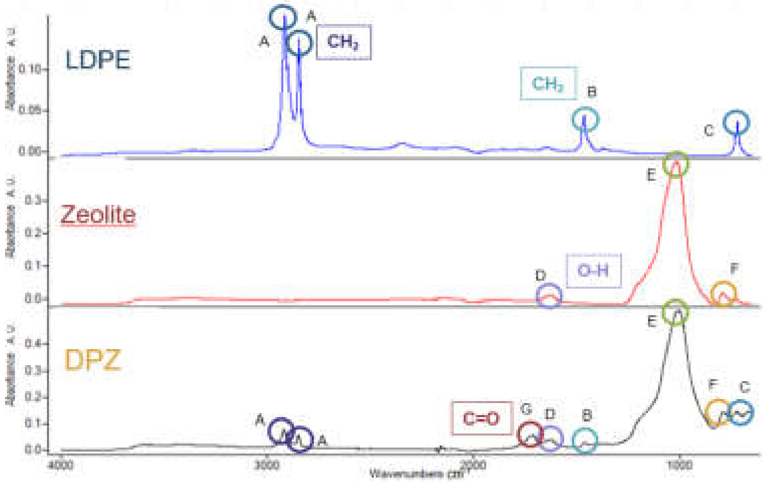
5.1 Material Characterization and Analysis

Going from dry blends made of zeolite and grinded LDPE (1:1) a new material was prepared by a simple dispersion in solid state thanks to acetone. These compounds are sufficiently well dispersed to have a homogeneous degradation and transformation to DPZ. Figure 4 shows the different states on the preparation of the materials. When zeolite is preheated no changes were observed at simple sight keeping its light brown appearance (Figure 4b) while after the thermal degradation of LDPE it became a yellow solid material (Figure 4c). DPZ-0 is observed as a dry blend with a light brown color given by the presence of the zeolite (Figure 4d) and DPZ-2 to DPZ-6 are presented as products that changed from light brown to dark brown when the time of degradation was increased (Figure 4e). After the phase separations, ZAE materials are observed as dark brown powders (Figure 4f) and WAX products as yellow waxes.

Figure 4. Different States of Preparation of Materials: a) LDPE Triturated, b) HZ, c) LDPE Degraded, d) Process of Formation of DPZ-0, e) DPZ-4, f) ZAE-4 and g) WAX-4.

FT-IR analysis shows the structural characteristics of the new material compared to the parents (Figure 5). LDPE as raw material shows the four characteristically bands that belong to the stretching, bending and rocking of CH_2 group in accordance with literature [28,139]. The bonds found on zeolite are characteristic of clinoptilolite, where Lewis acid sites, asymmetric and symmetric stretching vibrations are observed at 1625, 1010 and 791 cm^{-1}, respectively [109,128,140]. More proofs of structural characteristics will be given by XRD. All parent signals from zeolite and LDPE are observed in the FT-IR spectra of DPZ-

4. A disminution in PE signs present in DPZ in comparission of LDPE predecessor are attributed to the presence of zeolite [139]. A new band is observed in DPZ-a spectra caused by a C=O stretching. This carbonyl group is product of the oxidation of PE during a thermal treatment [139,141,142].



Wavenumber (cm^{-1})	Signal	Id
	LDPE	
2920,2851	Stretching CH_2	A
1464	Bending CH_2	B
719	Rocking CH_2	C
	Zeolite	
1625	O-H	D
1010	Si-O-Si	E
791	O-Si-O	F
	DPZ-4	
2920, 2851	Stretching CH_2	A
1715	Stretching C=O	G
1625	O-H	D
1464	Bending CH_2	B
1010	Si-O-Si	E
791	O-Si-O	F
719	Rocking	C

Figure 5. FT-IR Spectra of LDPE, Zeolite and DPZ-4.

Different authors have reported a catalytic degradation pathway that begins with a heat effect on the polymer causing a random breakage of C-C that reduces the length of the polymer and produces hydrocarbon radicals [26]. Once the polymer has been decomposed into lower mass oligomers (C30-C80) they can go inside the zeolite and react with the acid sites [95,110]. To follow this pathway is the main interest in the production of the DPZ where LDPE that is being degraded can penetrate and stay inside the porous structure of the zeolite. This behavior is of high relevance for the properties of the material to capture diesel, given that it should leave open free pores of the zeolite. Results seen by XRD, DSC and TGA support this mechanism.

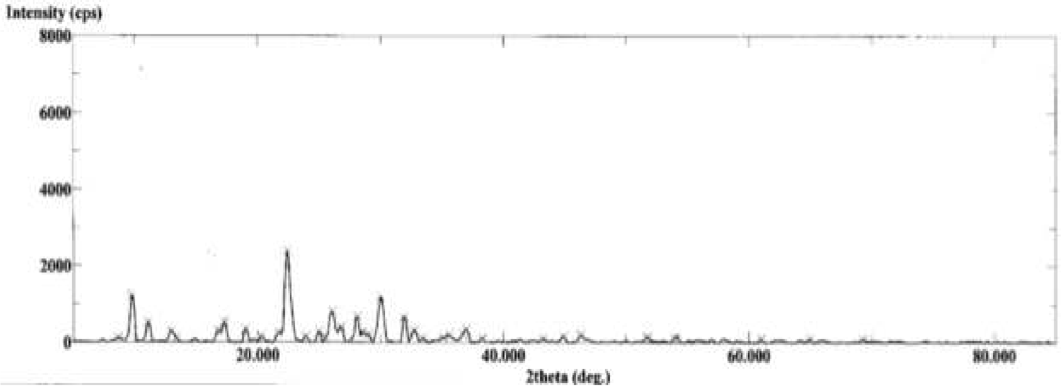


Figure 6. XRD Pattern Obtained from HZ sample.

The x-ray pattern of the zeolite (Figure 6) matches to clinoptilolite in accordance to the diffractogram presented by Bandura et al [24]. The evolution of the diffractograms of DPZs powders (Figure 7) show the PE crystalline signature (2 peaks at 2θ=20, 24deg observed in Figure 8 presented in DPZ-0 and DPZ-2. In addition, when DPZ diffractograms are superpositioned, they exhibit some modified peaks in intensity and shape; e.g. DPZ-0 to DPZ-6 in the ranges of 2q [22 – 30deg] and [17 – 20deg]. Also, all ZAEs still clearly show PE-peaks confirming that extraction of the PE is not total due to an incomplete degradation of it and insolubility of PE whereas waxes are soluble (Figure 8). These results are supported and correlated to the DSC thermograms of the same compounds.

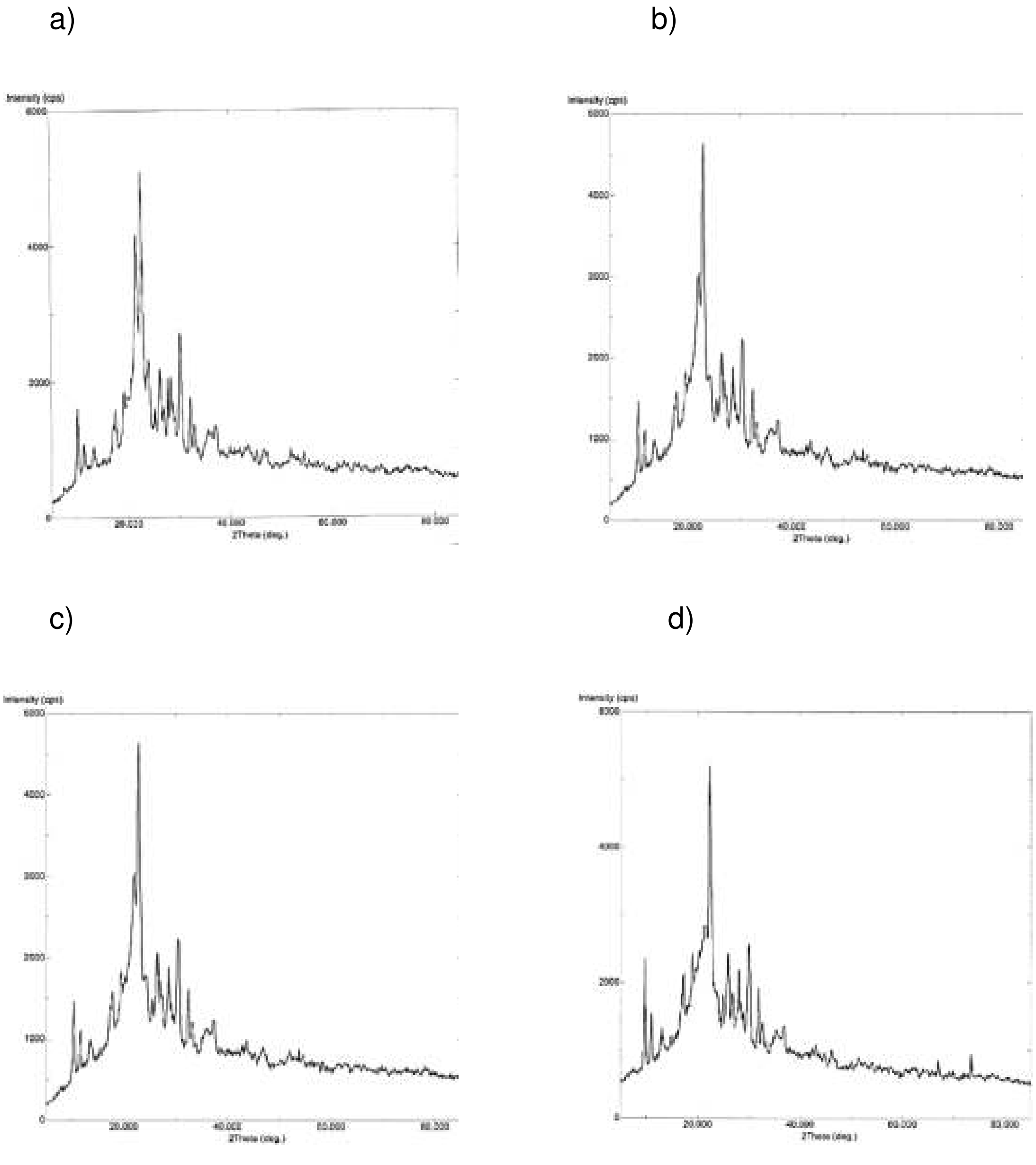


Figure 7. XRD Patterns of a) DPZ-0, b) DPZ-2, c) DPZ-4 and d) DPZ-6.

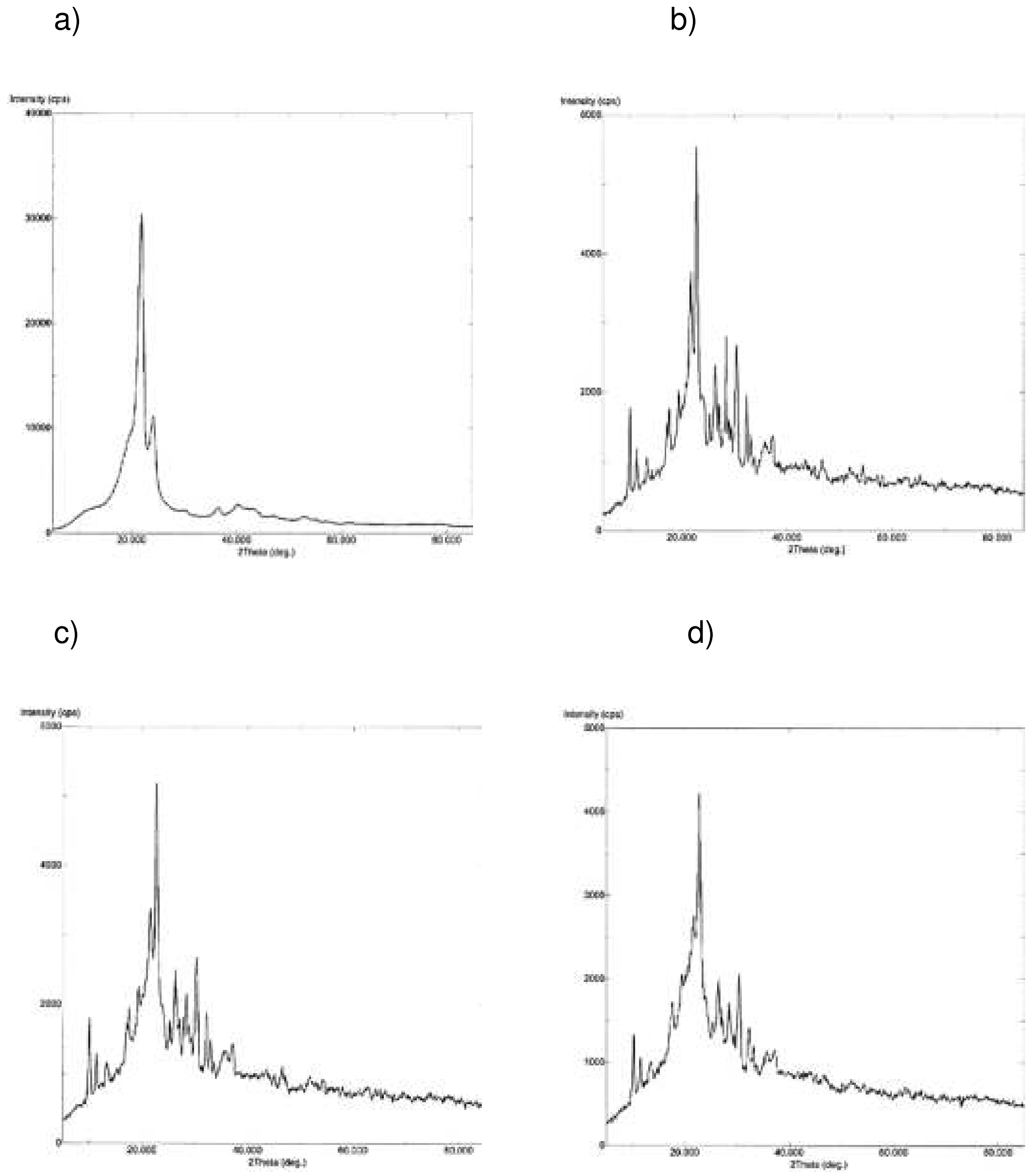


Figure 8. XRD Pattern of a) LDPE, b) ZAE-2, c) ZAE-4 and d) ZAE-6.

In Table 4 is observed that molar masses of PE-degraded products and waxes extracted from DPZ are logically decreasing with time. In the manufacture conditions of DPZ at 200 °C for 2 to 6 h, middle molar mass is obtained (~50 000 down to ~2000 g/mol). The original LDPE is a large bimodal distribution polymer formed mainly by two types of chain of different size, by observing two main overlapping peaks in the chromatogram, with molecular masses reported (Mn, Mw). Each peak of LDPE has a rather narrow (and ‘fictive’) polydispersity index (PD) of 1.7 and 1.4 respectively and Mw values of 136,300 and 11,700 g/mol. When giving thermal treatment to this PE at 200 °C partial degradation occurs, but the two peaks behave differently, that is, the lower molar mass peak is first decreasing and so is mainly affected by degradation. As observed in table 4, the chains that originally had Mw of 136300 g/mol are degraded down to 99100 g/mol with two hours of treatment. Those that had 11700 g/mol fall to 5730 g/mol, which indicates that within the cavities of the zeolite, the smallest molar mass chains accessible to cavities are preferentially degraded. LDPE is still present in DPZ-2, which was not soluble in TCB, and so not completely extracted, demonstrating the difference of behavior compared to WAX-4 and WAX-6.

Table 4. Polidispersity Index and Changes in Mn and Mw*
Depending on the Time of Preparation of DPZ.

Sample	Mn (g/mol)	Mw (g/mol)	PD
LDPE	79800 8250	136300 11700	1.7 1.4
WAX-2	45700 4300	99100 5730	2.2 1.3
WAX-4	62500 5720	98300 9530	1.6 1.7
WAX-6	60600 5420	96900 8470	1.6 1.6

*The distribution shows two peaks. Integration is made on each peak although they are shouldering.

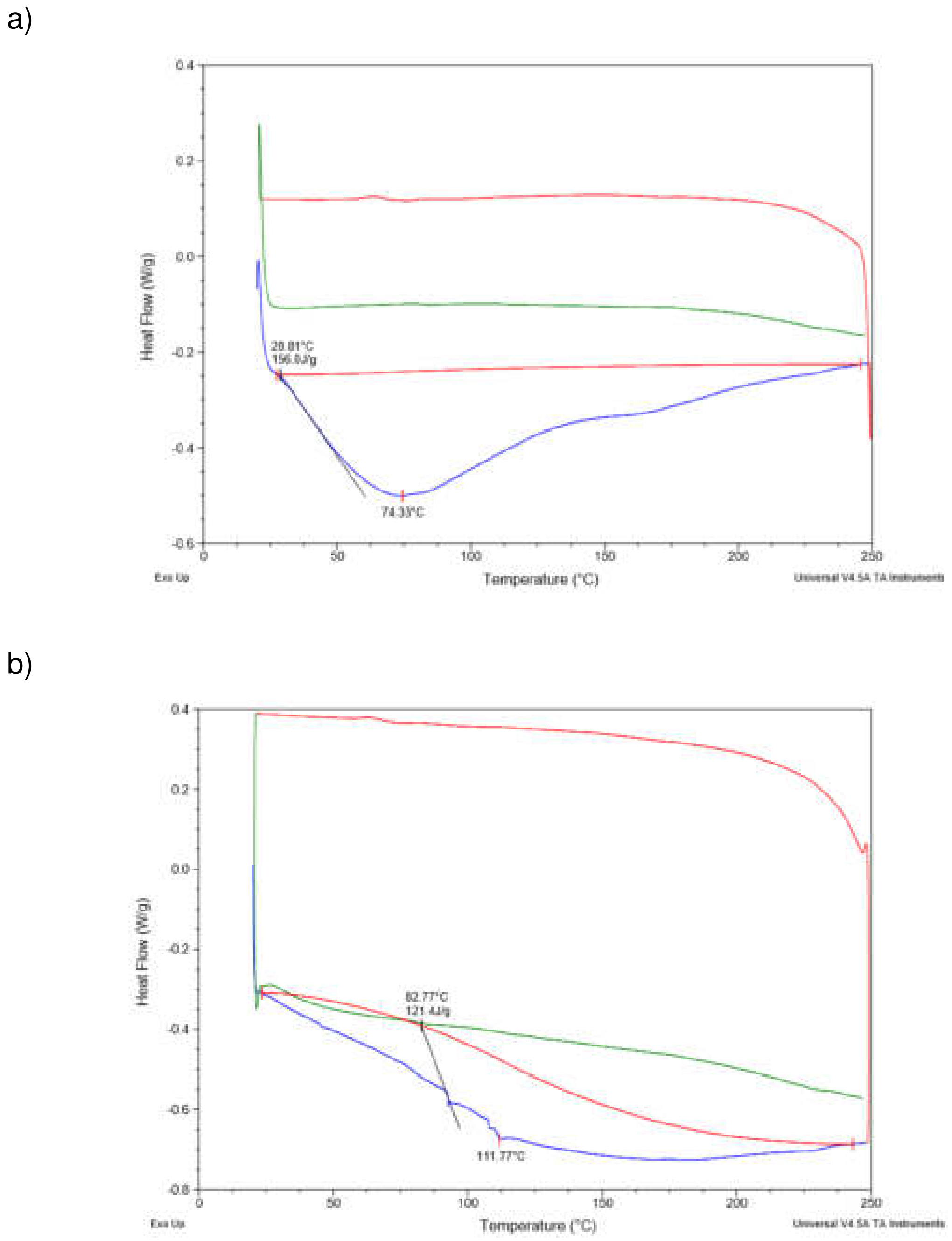


Figure 9. DSC Heating and Cooling Thermograms for a) ZEO and b) HZ.

In the shorter chains' distribution, a random phenomenon of recombination is present [143]. It is expected that the recombination occurs in shorter chains due to the higher probability that they must react with each other by combining free radicals present in the chains.

The preparation of DPZ was chosen to be only at 200 °C and for a maximum time of 6 h because higher temperatures and longer times can cause the total cracking of LDPE into small hydrocarbon molecules no larger than C8 [28,106].

The need to preheat the zeolite as a previous step in the formation of the DPZ is confirmed with the DSC graphs (Figure 9), were the HZ does not present heat exchange between 20 and 250 °C against the not heated zeolite that shows a broad water evaporation endotherm between 50 and 175 °C. This observation is also provided by the TGA results.

Figure 10 shows the classical melting range of LDPE extending from 75 to 130 °C with a 38 % crystallinity given that 290 J/g is enthalpy of 100 % crystal PE (See Table 5 for temperature peaks and enthalpies). When all DPZ are compared by DSC (Figure 10) it is noted a larger melting range of the PE from DPZ-2 to DPZ-6 compared to DPZ-0 with endotherm starting at 50 °C. The exothermic crystallization range of DPZ shows multiple maximum peaks due to molecular chains distribution. The behavior of all DPZ follows a melting and crystallization moving to lower temperatures caused by the degradation of the LDPE until it reaches an enthalpy value that can’t be detectable in DPZ-6. This same tendency is observed in all WAX products, proving that the hot-extracted products from zeolite are degraded PE oligomers and waxes. Finally, the ZAE compounds (Figure 11) show traces of PE on DSC thermograms in correlation with their XRD patterns. Meanwhile, it is observed that PE peak intensity is logically decreasing upon evolution of ZAE compounds (2 – 6 h).

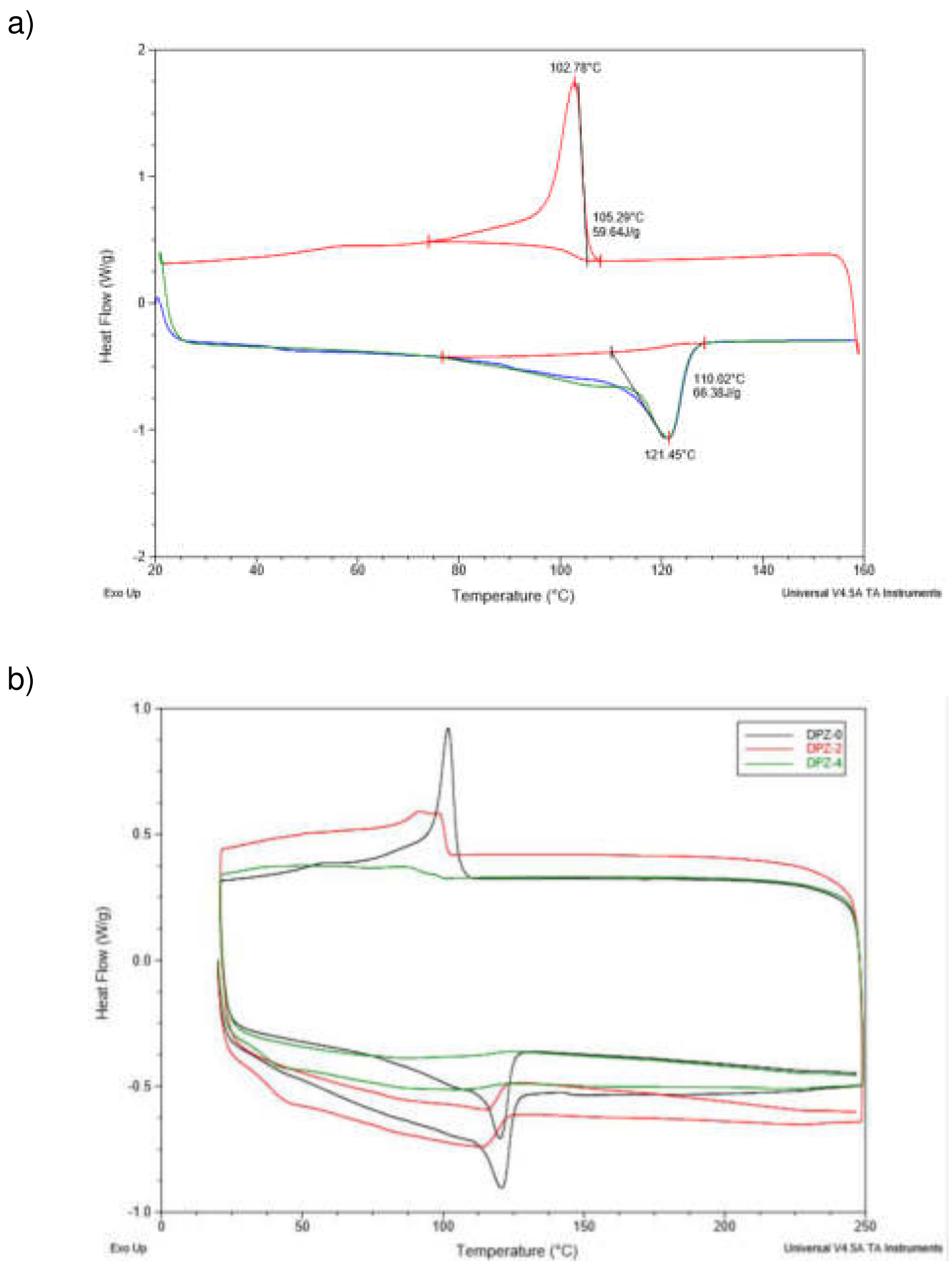


Figure 10. DSC Heating and Cooling Thermogram for a) LDPE and b) DPZ Products.

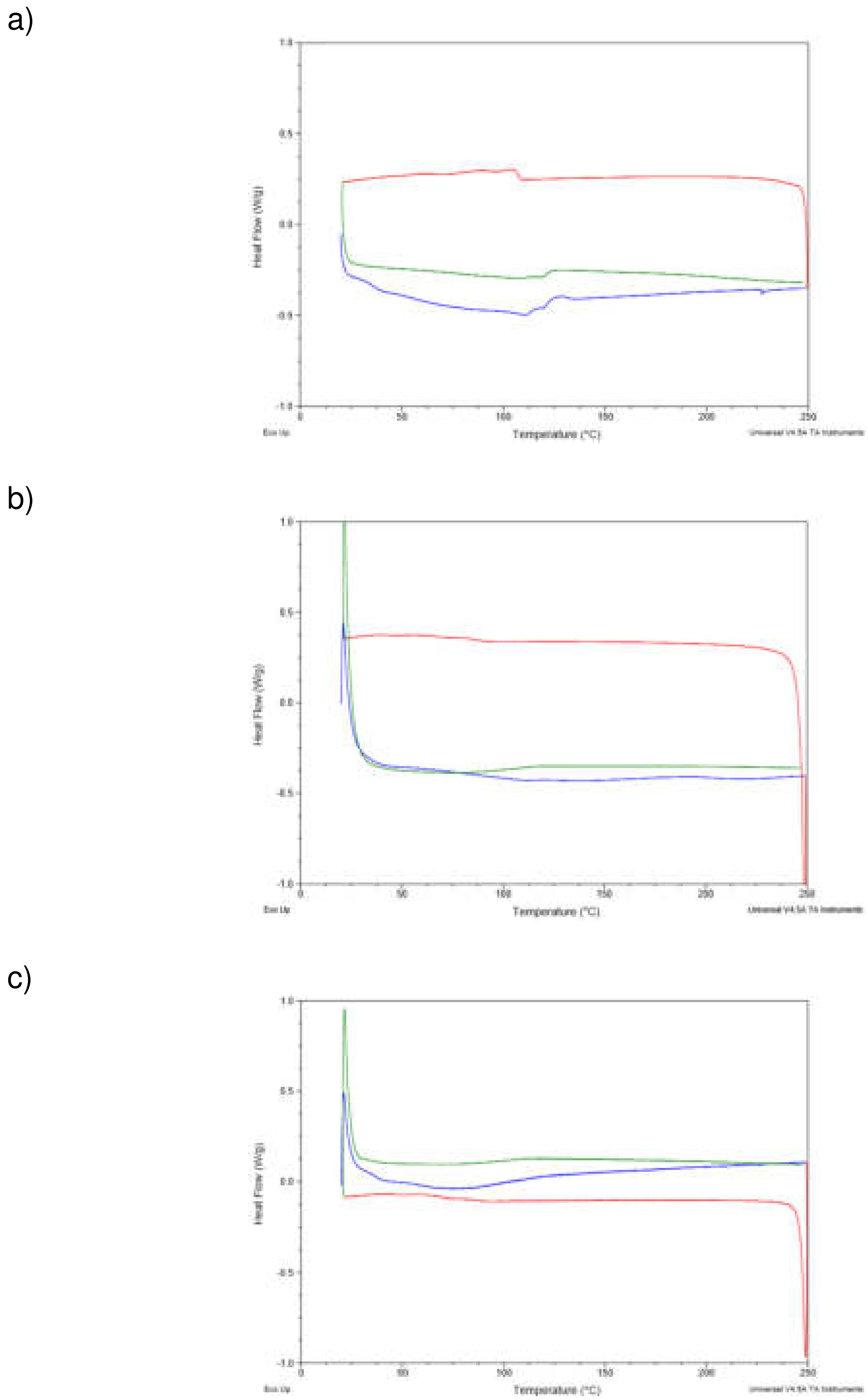


Figure 11. DSC Heating and Cooling Thermogram for a) ZAE-2, b) ZAE-4 and c) ZAE-6.

Table 5. Melting and Crystallization (25-250 °C) Peak Temperatures ($T_{m\ or\ c}$) and Enthalpies ($\Delta H^{m\ or\ c}$) Measured by DSC.

Sample	T_m (°C)	ΔH^m (J/g)	T_c (°C)	ΔH^c (J/g)
LDPE	121	111.2	103	105.0
LDPEdeg	122	62.8	98	73.8
DPZ-0	120	36.1	102	45.6
DPZ-2	115	22.9	92	37.7
DPZ-4	87	6.0	85	14.1
DPZ-6	-	-	-	-
ZAE-2	108	10.0	103	14.3
ZAE-4	-	-	-	-
ZAE-6	-	-	-	-
WAX-2	79	14	78	7.4
WAX-4	-	-	88	14.7
WAX-6	-	-	-	-

All above remarks prove insertion of molecules inside the crystalline mineral structure of the zeolite by intercalation. Parts of these inserted organic molecules are oligomers with crystalline zones as attested by their x-ray signature and DSC traces (with a lower melting point than PE).

The last part of the characterization was to follow the thermal degradations by TGA (Figure 12). Beginning with the raw materials, zeolite and HZ were compared. There is a 9 % of weight lost in the raw zeolite in air or N_2 with a single derivative peak at 200 °C (temperature at which zeolite is activated) compared to 7 % weight loss from HZ, this demonstrates that zeolite regains water very quickly so that HZ should be scanned by TGA just after drying. Neat PE on a heating ramp at 10 °C/min totally loses its 100 % mass reaching 500 °C in air and nitrogen, with different start degradation points and slopes that indicate not the same degradation mechanisms. When DPZ curves are examined both kind of mass loss are presented, one due to the PE degradation and the other one from hygroscopic water evaporated from the zeolite.

On the N_2 heating ramp, DPZ-0 first shows a water loss then an abrupt mass loss from 400 to 490 °C corresponding to PE loss; the final total mass loss (54%) corresponds exactly to DPZ drying and complete PE degradation mentioned before. The single derivative peak is in favor of one mechanism of PE degradation in N_2. DPZ-2 and DPZ-4 have a similar behavior (final mass about 50%) meaning no mass loss at 200 °C during their preparation, and no volatile compounds were created having a partial degradation of LDPE that does not reach low molar mass hydrocarbons. This also means that all degraded molecules from PE are remaining totally inside DPZ or around zeolite grains. Furthermore, before the single degradation main peak (above 400 °C), a shoulder appears at around 350 °C on DPZ-2 and is increasing with DPZ preparation time and it is correlated to a major formation of wax during production of DPZ. When we consider the width of the derivative of the single degradation main peak (400 °C) by tangents method, it is observed that the longer the preparation time of DPZ, the broader this peak. In addition, the wax degradation peak enlarges but keeps always centered at around at 350 °C.

On a heating ramp in air, more mechanisms are present as attested by the various derivative peaks. TGA shows a main degradation sharp peak 425 – 450 °C plus a wax degradation peak around 350 °C. Only DPZ-6 starts to show a small mass loss before TGA analysis, that could indicate some escaped volatiles during DPZ preparation. This means that there is an optimal time for PE catalytic degradation in zeolite, that should not reach six hours of degradation in order to keep degraded products in the zeolite. Finally, on the isothermal plateau at 200 °C, the TGA 6h degradation curve of DPZ-0 induces the immediate and continuous degradation of PE exhibited by a decay of mass until losing 14 % of weight, consistent with 4 % from DPZ and 10 % from PE. Indicating a 90 % of PE inside the zeolite after 6 h.

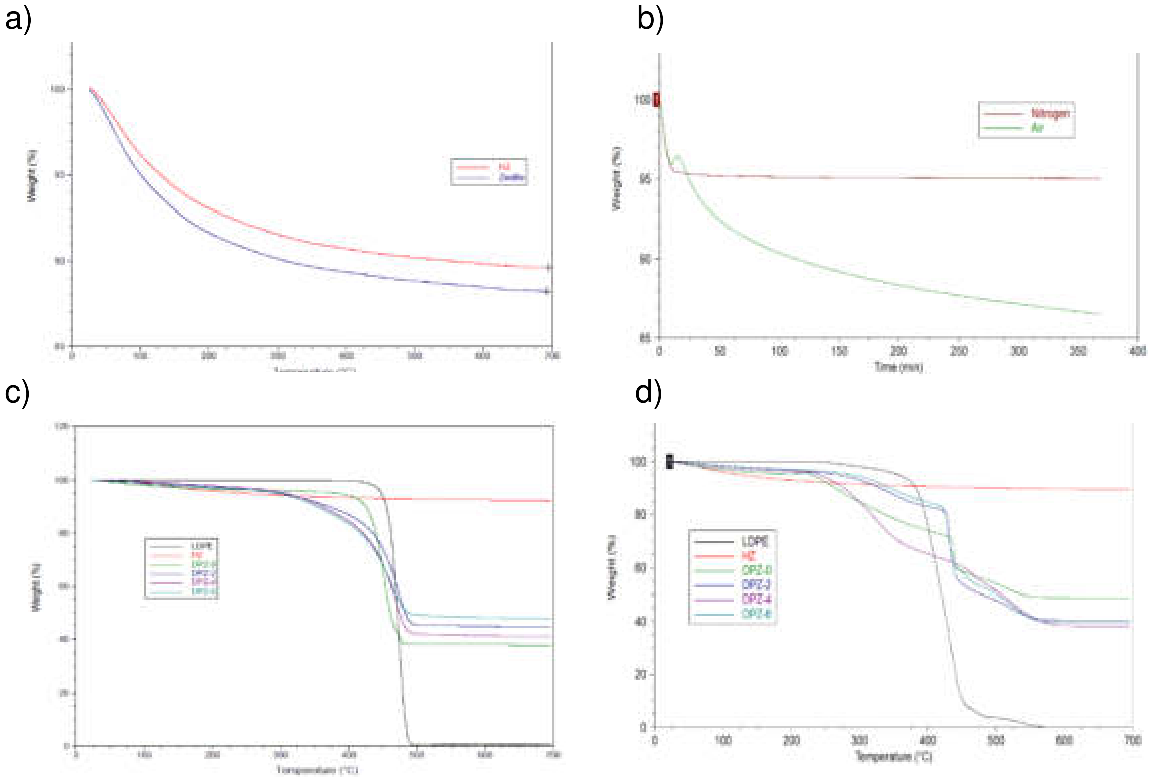


Figure 12. TGA of a) Zeolite and HZ Under Air; b) DPZ-0 Degraded During 6 h at 200 °C Under Nitrogen and Air; LDPE, HZ, DPZ-0, DPZ-2, DPZ-4 and DPZ-6 Under c) Nitrogen and d) Air.

5.2 Sorbent Selection by TGA Analysis

The compounds are first tested towards their ability to absorb/adsorb neat diesel in the S+D system and then towards their ability to separate diesel from water (selectivity) in the S+D/W system. In S+D system, all materials change to a darkest color given for the presence of diesel except for LDPE, which kept the same appearance after being in contact with diesel for 18 h (Figure 13). In the selectivity essays, the favorable characteristics of a sorbent as swelling and buoyancy were observed in DPZ-2,4,6 and ZAE-2,4,6. In the case of DPZ-0, this mixture was divided in the two parent materials as seen in (Figure 14).

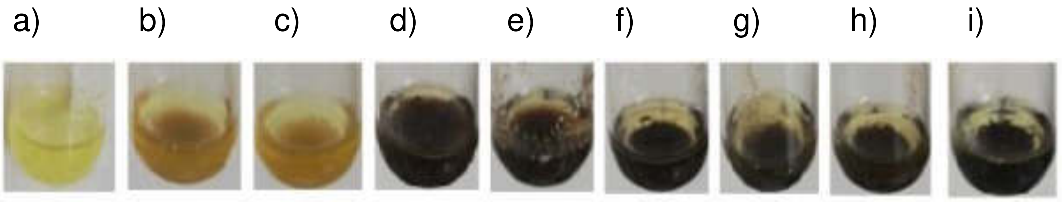


Figure 13. S+D Systems for a) LDPE, b) ZEO, c) DPZ-0, d) DPZ-2, e) DPZ-4, f) DPZ-6, g) ZAE-2, h) ZAE-4 and i) ZAE-6.

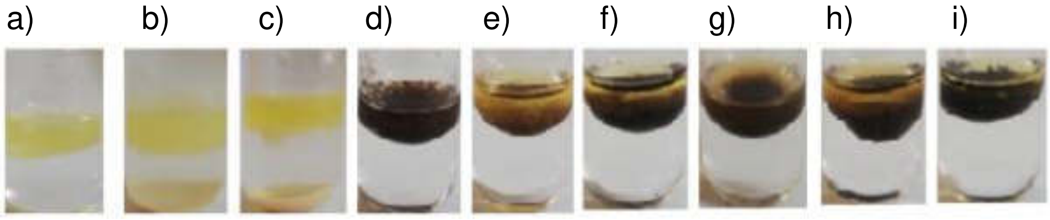


Figure 14. S+D/W Systems for a) LDPE; b) ZEO, c) DPZ-0, d) DPZ-2, e) DPZ-4, f) DPZ-6, g) ZAE-2, h) ZAE-4 and i) ZAE-6.

To quantify the diesel absorbed the mass loss peaks were identified in the TGA curves. Several events in the TGA analysis that occur in separated ranges of temperature are distinguished in Figure 15. The first range up to 115 °C comprise water evaporation; PE degradation is marked at 200 °C; the range of diesel evaporation is 115 to 275 °C; outside PE-200 °C-degraded products thermolysis is in a range of 275 to 400 °C and inside PE-200°C-degraded products thermolysis begins after 400 °C.

In order to explain the sorption capacity of DPZ-*n*, one must consider that PE degradation products may locate both outside and inside zeolite and that zeolite is partially “filled” with hydrocarbon molecules (called PE-degraded products). This is explained in Figure 21 where possible structure of DPZ sorbent and diesel removal is shown. DPZ’s are granular stackings (green color) partially filled with PE-degraded products (waxes in purple color), where these medium molar mass hydrocarbon solid compounds may be found either inside zeolite micro pores (red color) or between the DPZ grains (intergranular position, grey color) depending on their molar mass.

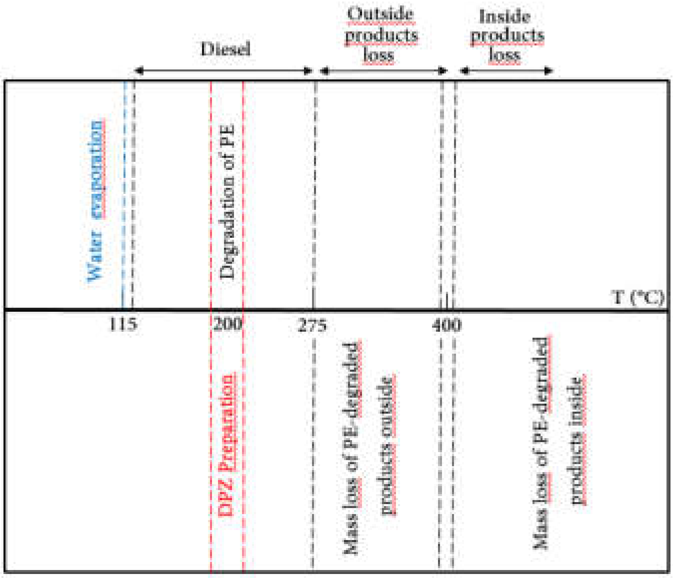


Figure 15. Thermal Events in TGA Analysis.

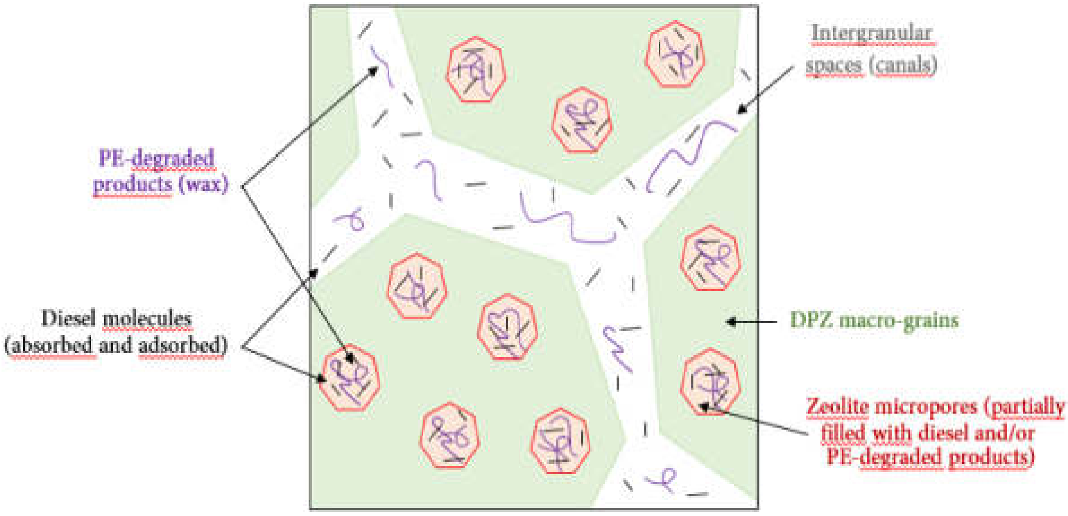


Figure 16. Absorption/Adsorption Mechanism in the DPZ Structure.

Porosities come from zeolite micro pores and macro porosities in DPZ's intergranular voids (or canals). Diesel molecules are (black color) absorbed and/or adsorbed in the different free areas (zeolite pores or intergranular canals) due to capillary effects and Van der Waals interactions.

Figure 17, Table 6 and Table 7 give TGA traces and values of sorbent diesel capacities of the different materials. All diesel outside or diesel weakly bonded to the sorbents was absorbed by the filter paper. In the S+D systems, the ZEO and DPZ-2 absorb the same apparent amount of diesel (39 %). But when water is applied to the system, the selectivity for diesel of DPZ material against water is clearly notorious.

DPZ is a combination of light porous hydrophobic material. If there is too many PE-degraded molecules in zeolites (e.g. DPZ-6), diesel is poorly removed, pores are clogged or blocked; if there are not enough PE-degraded molecules in zeolites (e.g DPZ-0), the sorbent is not enough diesel-philic and not enough cohesive (PE and zeolite phases are seggregated). In both systems DPZ-2 showed the highest capacities of diesel removal being capable of separate the diesel present in water.

TABLE 6. TGA weight loss measurement of diesel in S+D systems

Sorbent	TGA weight loss (%)
LDPE	12
Zeolite	39
DPZ-0	25
DPZ-2	39
DPZ-4	29
DPZ-6	23
ZAE-2	25
ZAE-4	24
ZAE-6	14

TABLE 7. TGA weight loss measurement of diesel in S+D/W systems

Sorbent	TGA weight loss (%)
LDPE	14
Zeolite	5
DPZ-0	6
DPZ-2	45
DPZ-4	39
DPZ-6	31
ZAE-2	15
ZAE-4	11
ZAE-6	5

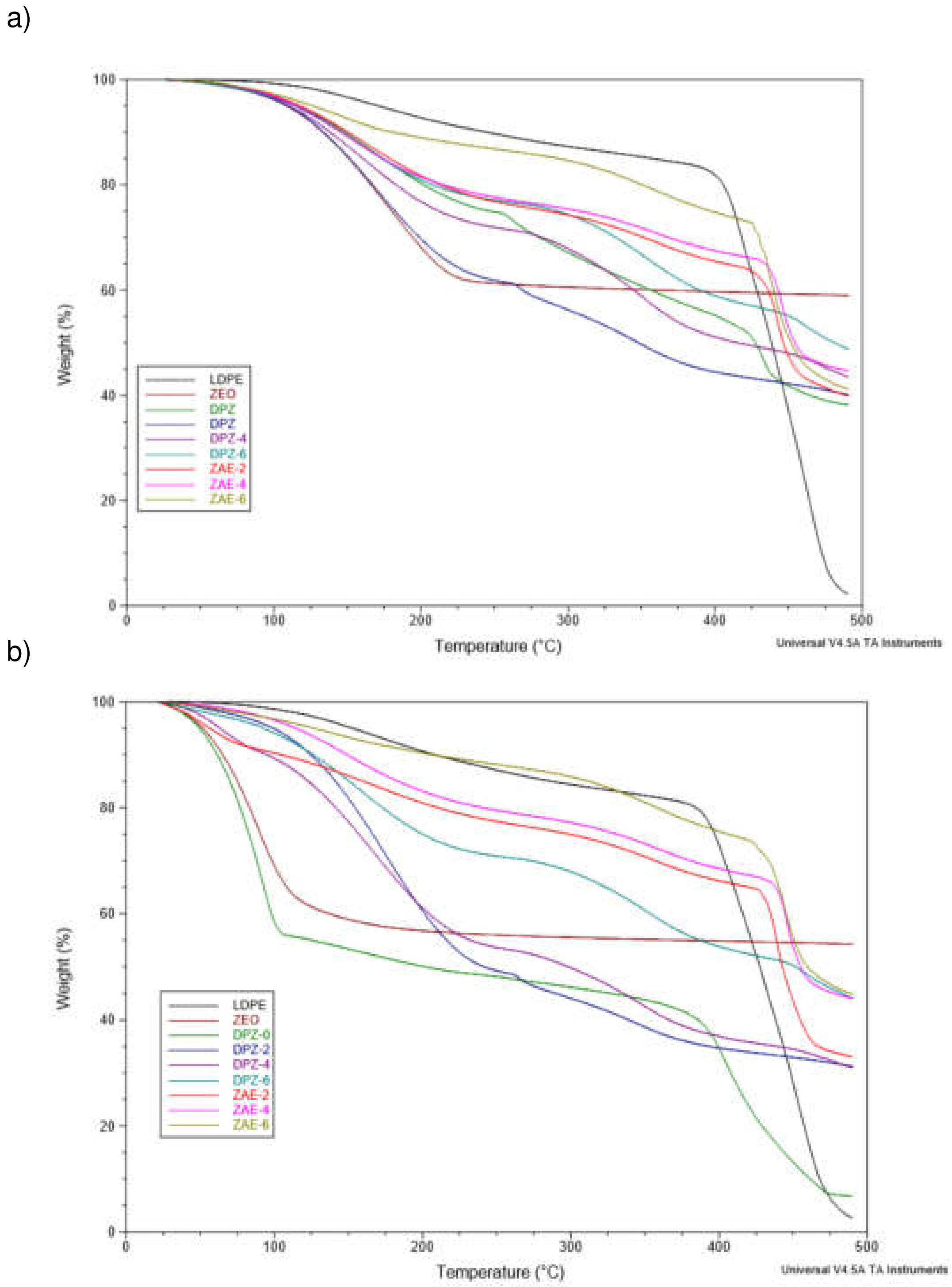


Figure 17. TGA of Sorbents in a) S+D System and b) S+D/W System.

5.3 GC-FID Sorption Analysis

Good linearity and correlation were obtained in the calibration curve (Figure 18) with the standards mentioned in table 8. The calibration curve presents a high significative correlation based on the correlation coefficient (R2) which is 0.98, nearly 1. This is a similar result as the calculates by different authors [35,144]. The RSD obtained is 9%, a very low percentage compared to values of 20% reported in literature [35] proof of a trustable concentration range to quantify diesel that can also be considered as a quantification technique for traces [145] being proof of a trustable concentration range to quantify diesel.

Table 8. Standards Used to Prepare the Calibration Curve.

Standard concentration	Intensity (mV)
100	0.1843
300	0.3229
530	0.4018
700	0.5872
1020	0.8147

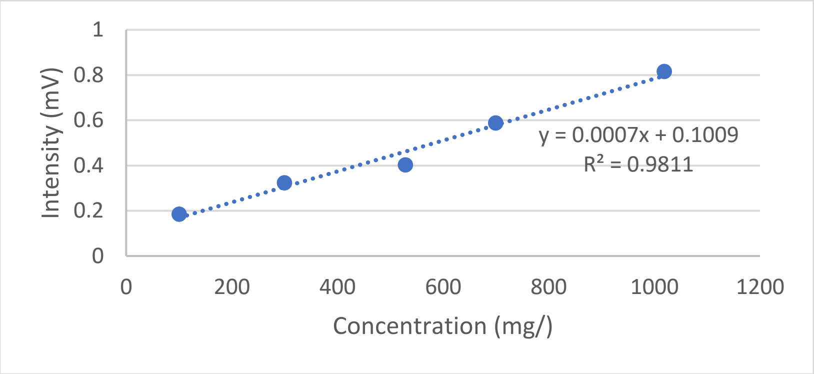


Figure 18. Diesel Calibration Curve on GC-FID Obtained with the Standards of Table 8.

The LLE was carried out by multiple step extractions in accordance to literature. Recovery percentages were 99 and 86% for the standards of 490 and 1000 mg/g, respectively. This high percentages fit with the EPA requirements where a validated extraction technique should present recovery percentage higher than 70% [35]. These values are obtained for the easy separation because diesel and water present opposite properties that facilitate the migration of diesel to CH_2Cl_2 [146]. Finally, the LOD and LOQ for the presented technique were 121 and 124 mg/g, respectively.

Our intention of designing a two factorial block was in order to determine the dose and temperature to improve the diesel sorption. As seen in table 9 most of the experiments resulted in a final concentration under the limits of detection and quantification so no statistical methodologies could be applied.

TABLE 9. Screening of Temperature and Sorbent Dose.

Temperature (°C)	Sorbent (g)		
	0.01	0.03	0.05
25	<LOD/LOQ	<LOD/LOQ	<LOD/LOQ
35	203	<LOD/LOQ	<LOD/LOQ

6

PRELIMINAR CONCLUSIONS

The degradation of low-density polyethylene in the presence of zeolite was achieved by forming short chains soluble in TCB. The correlated results obtained from the different analytical techniques are coherent and prove that middle molar mass oligomers presented as waxes are formed and remain into or around the zeolite during its preparation. These degraded compounds have enough interactions to the zeolite to form cohesive but porous grains. The formation of low molar mass hydrocarbons was avoid being able to have enough interactions with diesel. In the rather mild conditions chosen (200 °C), PE cannot be totally transformed into degraded products, but shows the importance of middle molar mass degraded compounds to form a new sorbent. This porous hydrophobic, water floating, diesel-philic acts as a sorbent with both favorable thermodynamic interactions, capillarity and low density.

The gas chromatography method established for the quantification of diesel presents validation parameters in acceptable ranges for the project objectives.

7

AUTOBIOGRAPHY

Samantha Molina Flores

To obtain the Grade of MASTER IN SCIENCE
with orientation in chemical analytical chemistry

Thesis

DIESEL REMOVAL FROM WATER BODIES USING A NEW RECYCLED SORBENT BASED ON LOW-DENSITY POLYETHYLENE DEGRADED WITH ZEOLITE.

Field of Study:

Chemistry

Biography:

Born in Monterrey, Nuevo Leon in October 2nd, 1995. Daughter of Maria de Jesus Flores Chavez and Abel Molina Rodriguez.

License:

Universidad Autonoma de Nuevo Leon with the grade of Genomic Biotechnology in 2017.

8

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