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# Polymer Materials & Waste Industrial Products might be Dangerous for Destroying the Forests in Türkiye: An Overview of Climate Changing in Viewpoint of Bio Thermochemical Analysis

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**Abstract:** Cleaning and saving the forest is related to managing and utilizing forests' biodiversity, productivity, and considering the relevant environment. Plastic waste management is now seen as an important goal for sustainable forest use as well as incorporating recycled plastics into products. Another way that industries impact wildlife and forests is by releasing additives such as industrial gases, organic & inorganics materials, plastic & resins, fertilizers & alkalies, and chlorine. Polymer wastes manage to enter into and harm numerous biological functions of animals. In this work, the concept of sustainable Türkiye's forest practices and addressing the impact of plastic waste on the forests and environment before and during the COVID-19 epidemic are discussed along with current sources of those mentioned materials wastes that manage to enter the environment. Through this work, the data of bio thermochemistry and thermodynamics calculations of such polymers have been investigated to exhibit the range of sustainability and unsustainability of those mentioned polymers and resins in the environment due to forest climate change. Since the Türkiye chemical industry is one of the most important industrial factors, their production contributes in similar proportions to greenhouse gas emissions. Interestingly, low data on energy usage in the factories and chemical industry is available in the public domain. Ethylene production is the major product in terms of the production volume of the petrochemical industry. Nitrogenous fertilizer production is a very energy-intensive industry, producing a variety of fertilizers and other nitrogen compounds. In addition, ammonia, chlorine, and caustic soda are the most important mediator chemical material used as the main compound for almost all products.

**Keywords:** biochemical products in Türkiye; forests in Türkiye; climate changing; greenhouse gas emissions in Türkiye.



## 1. Introduction

### *1.1. Pollution of hydrocarbon in Türkiye.*

In summer, electricity usage increases extremely because of keeping cool air condition and food in industrial refrigerators. Most electricity is produced from coal, gas, and hydropower; hydroelectricity is sent from the east to the western cities in Türkiye. Although the electricity prices are state-controlled, the cost of imported gas heavily influences wholesale prices. $CO_2$ produced from basic chemical production decreased from the previous year (from 2021 compared with 2020), resulting from production declines due to the Covid-19 crisis. Nevertheless, this still increased annually from 2015. In the Net Zero produced by 2050 plan, emissions from basic chemical production peak in a few years next and will decrease by 2030, despite strong growth in demand. Therefore, it is necessary to control the $CO_2$ produced from chemical production via several approaches, such as keeping the forest, controlling the waste of heat in the building, and using and disposing of chemical products. The chemical centers have the most industrial usage of oil, gas, and energy.

Nevertheless, it is the third center in direct $CO_2$ emissions, behind cement, iron, and steel. This is due to half of the chemical subsector's energy input being consumed as feedstock fuel used as raw material input rather than as a source of energy. The chemical centers are the largest energy consumed in industrial countries such as Germany, the USA, and Türkiye. The chemical industry is complex, encompassing the production of over fifty thousand chemical compounds. The industry is also an important part of the global economy, accounting for approximately 6% of global income and 10% of international trade [1]. The chemical industries generate several intermediate materials applied as the initial compounds for other chemical products. For instance, ethylene ($C_2H_4$), one of the most important bulk chemicals from an energy point-of-view, is applied as a crop in a reaction to produce plastics. Also, several reactions in the chemical products of Türkiye's industries generate different co-products that cause energy in the chemical industry to be more intricate than in other centers. In this paper, we study the energy consumption of the Türkiye chemical industries to answer the question, "How the Turkish forest can be affected by chemical products from industries"? We analyze current energy consumption and production levels, which can be used to develop a detailed baseline energy consumption and prevent deforestation and environmental degradation for several chemicals such as ethane, naphtha, gas oil, ethylene, ammonia, and chlorine. The energy intensities baseline of three major bulk chemicals, i.e., ethylene, ammonia, and nitrogenous fertilizers, will be useful based on these detailed analyses of the potential for energy efficiency improvement and carbon dioxide emission reduction in Türkiye. Coal, truck, and tractors are approximately half of Türkiye's five hundred million tons of annual greenhouse gas emissions mostly carbon dioxide with some methane. These are part of the cause of climate change in Türkiye. Besides coal and gasoline, CNG gas is an important matter burnt in Türkiye's gas-fired power stations, homes, and workplaces. In other words, cows belched methane, producing half of the greenhouse gas from agriculture. Although in economics, subsidizing coal-fired power plants has been paid for, the owners believe even with this subsidizing, their activities would be gradually stopped and closed due to the wind power and solar systems that are much cheaper and cleaner [2, 3]. Türkiye's gas-producing contribution to the global greenhouse (GGH) is about one percent, which means each person is around 6 tons a year (equal to the world average) [2-4]. Türkiye removes and cleans approximately a fifth of its emissions through its forests. Although the government supports reforestation, electric vehicle manufacturing, and low-carbon electricity generation, it must decrease more. Türkiye's climate and energy policies will control high-carbon products, such as cement and electricity, by paying carbon tariffs.

### *1.2. Energy use in the chemical industry.*

Carbon dioxide ($CO_2$) of fossil fuels is the most section of greenhouse gas (GHG) emissions. Based on International Energy Agency (IEA) reports, in 2019, Türkiye had 5.1 tons of $CO_2$ emitted per person, which was around 1.1% of global $CO_2$ (Figure 1-a) [5]. Based on the Climate TRACE report in 2020, the GGH production in Türkiye was approximately the same as in 2019, including 24% from power generation, 21% from manufacturing, 14% from buildings, 11% from waste, and 9% from agriculture [6,7]. These amounts can be compared with $CO_2$ emissions by U.S. Manufacturing from 10 years between 1985-1994 through Source: *EIA (1997); EIA (1996); BOC (1998)* (Figure 1-b). The U.S. Survey yields energy consumption data of chemicals subsection that accounted for the largest contribution of primary energies (Table 1), including 1- industrial organic chemicals, industrial inorganic chemicals, plastic materials & resins, and nitrogenous fertilizers, industrial gases, alkalis, and chlorine. These exhibit several highly energy-intensive production processes within these subsectors often used to produce intermediate chemicals.

**Table 1.** Primary Energy Use, Shipments, Value Added, Carbon Dioxide ($CO_2$) Emissions, for Selected U.S. Chemicals Subsectors in 1994.

| **Chemical subsection** | **SIC code** | **Primary energies** | **Co₂ Emission (MtC)** |
|---|---|---|---|
| Industrial gases | 2813 | 364 | 4 |
| Organic materials | 2869 | 1.653 | 25 |
| Inorganics materials | 2819 | 830 | 11 |
| Plastic & resins | 2821 | 518 | 7 |
| Fertilizers | 2873 | 344 | 10 |
| Alkalies & Chlorine | 2812 | 286 | 4 |
| others | | 1.146 | 16 |

It is notable that industrial organic chemicals accounted for the largest share of energy use in the chemicals sector as a whole. From an energy perspective, some of the key chemical products included within this category are ethylene and other steam-cracking derivatives (propylene, butadiene, and methanol). Currently, ethylene and its derivatives are important petrochemicals in any economics and feedstocks for many plastics and resin products, as well as fibers and detergents. For ethylene preparation, ethane or naphtha is heated in pyrolysis furnaces, segregated into gaseous materials, and rapidly cooled with high compensation. More severe processing conditions require more energy to crack but result in more co-product yields of methane, butadiene, benzene, and toluene [8]. From the viewpoint of MRV (Monitoring, reporting, and verification), the Turkish government's statistical institute obeys the United Nations Framework Convention on Climate Change (UNFCCC) reporting guidelines. In addition, it has been estimated this production is based on GGH information on the country's greenhouse gases [9].

Notably, emissions from fuels sold in Türkiye for international flights and whole abroad shipping are accounted for separately in reports to the UNFCCC. For instance, jet kerosene, supplied for international flights in 2019, was estimated 14 Mt $CO_2$, as well as diesel oil and residual fuel oil from international shipping were calculated at around 3 Mt [10, 11]. The International panels on climate change (IPCC) indicate three ways of measuring emissions. The first step is from global defaults, the second is via country-specific information, and the third can be done through detailed data for further simulation.

These categories can be selected based on several databases; for instance, lime production was an important key due to its quickly rising emissions [11]. Other items, such as cement production or a power plant that burns lignite, differ from mine to mine [11]. 506 Mt of GGH was emitted by Türkiye in 2019 [12-14], which is lower than the world average per person. Türkiye's cumulative $CO_2$ emissions are estimated at around 10 Gt, which is 0.6% of the world's cumulative total [9]. Türkiye's emissions can be looked at from different perspectives. For instance, a study by the Izmir University of Economics estimated that food "from farm to fork", accounts for about a third of national emissions [15, 16]. That is the same as the global emissions share of food [16]. Burning coal has the most rank of any kind of fossil-fuel emissions in Türkiye, and Türkiye's energy section emitted over 65% of the country's GGH, through electricity generation and also from the fuel of tracks in related transport. In contrast, industrial processes contributed somewhat around 15% of emissions, as did agriculture [11, 12, 15, 17].

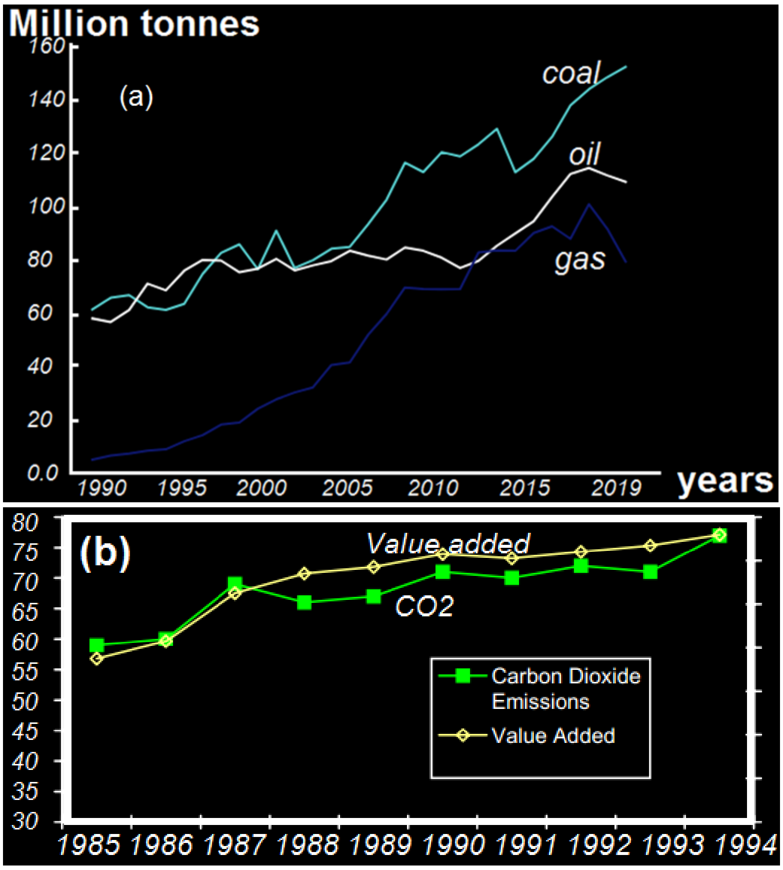



**Figure 1. (a)** $CO_2$ emitted by fossil fuels burning; (**b**) $CO_2$ emission by U.S. manufacturing from 10 years between 1985- 1994.

Although from 2023, Türkiye intends to increase gas production [18] largely, IEA called for fossil fuel-producing countries to include limiting methane leaks in their climate pledges [19-24]. Scheme 1 exhibits an image of haze from burning coal over apartment blocks pollution over Ankara, which indicates coal is still burnt to heat older buildings in cities.

**Scheme 1.** Air pollution over Ankara.

For solid fuels, around 1000 grams of $CO_2$ is emitted due to producing one KWh of electricity in Türkiye from each coal-fired power station [25]. The coal burning is mostly bituminous or hard coal, which an analysis of Turkish lignite exhibits large moisture, low yield, with huge $CO_2$ emission. In addition, $CH_4$ leaks from coal mines were equivalent to 7 Mt $CO_2$ in 2019 [26-28].

*1.3. Industrial organic chemicals pollution in Türkiye.*

Industrial organic chemicals are the largest share of energy use in the chemicals section. From an energy perspective, some of the key chemical products included within this category are ethylene and other steam-cracking derivatives (propylene and butadiene) and methanol. Ethylene and its derivatives are important petrochemicals in the Türkiye economy and feedstock for many plastics, resin products, fibers, and detergents. Ethylene is one of the largest chemicals produced, while propylene, after ethylene, is also an important chemical. Türkiye currently has an ethylene producer accounting in world installed capacity, and ethylene production has grown annually. Propylene has grown more rapidly in the last decade in Türkiye. In ethylene factories, alkane feedstocks like ethane or naphtha are heated in furnaces, separated into gaseous, and quickly cooled, compressed, and purified. Smaller feedstocks, same as ethane, produce higher ethylene yields. The larger molecules need higher temperatures and pressures for using heavier feedstocks and require more energy to crack. Still, they also result in a more co-product that yields methane, butadiene, benzene, and toluene. In the Türkiye, ethane remains the primary feedstock used in steam cracking, followed by propane, naphtha, and gas oil. Methanol is generated through the reaction of carbon monoxide and hydrogen. Although hydrogen needs significant energy use, methanol demand has been driven up in recent years, that it is due to the increasing demand for Methyl Tertiair-Butyl Ether (MTBE) as a reformulated gasoline additive, which is an advantage compared to the disadvantage of energy consumption. However, MTBE use in the Türkiye will stop in the predictable future due to water pollution problems. Industrial inorganic compounds are also the largest share of carbon emissions within the Türkiye chemicals and contain a wide variety of inorganic chemicals, including $H_2SO_4$, HCl, KOH, and $Al_2O_3$.

*1.4. Plastic materials, resins, gases, alkalis, and chlorine.*

The production of plastic materials accounts for a major percentage of carbon dioxide emissions due to primarily the large volume of production in Türkiye. Some of the main plastic products include [-$CH_2$-$CH_2$-]$_n$ or [$CH_3$-CH= $CH_2$$^{\cdots}$]$_n$, polystyrene, and PVC. Ethylene is the main molecule for using polyethylene manufacture. Estimates of per-ton energy requirements for polymerization processes are shown in Table 2 [29, 30].

**Table 2**. Energy requirements for plastics production (GJ $ton^{-1}$).

| Product | Estimate 1* | Estimate 2* |
|---|---|---|
| Polyethylene (LDPE) | 9.3 | 1.6 |
| Polypropylene | 10.5 | 1.2 |
| Polystyrene | 9.3 | 11.3 |
| Polyvinyl Chloride* | 11.6 | 9.9 |

*Estimate (1) is based on Lipinsky and Wesson [29]; Estimate 2 is based on Worrell et al. [30].

The growth rates of producing [-CH2-CH2-]n or [CH3-CH=CH2]n, polystyrene, and PVC over the last two decades are dangerous for climates. Plastic consumption has grown quickly at rates, particularly strong growth in PVC, polypropylene, and polyethylene. Industrial gases are approximately energy-intensive process. Around 6% of carbon dioxide emissions, nitrogen, and oxygen production, are typically the second and third largest chemicals produced mainly through cryogenic air separation, where the air is cooled and pressurized until it becomes a liquid with the various gases extracted through fractional distillation. However, other technologies, such as pressure swing absorption and membrane separation, are increasingly being used. Energy consumption for oxygen production has been estimated at 2.0 GJ/tonne [31].

Although ammonia production is a highly energy-intensive process, roughly 80% of $NH_3$ production is used as fertilizer feedstock [29]. Like methanol, ammonia is produced via high-pressure synthesis of gases ($CO_2$ and $H_2$). The $Cl_2$ gas is an important element for PVC preparation that has been growing rapidly over the past decade [29].

The $Cl_2$ gas is also used as a bleaching agent in pulping operations. The production of $Cl_2$ gas is a highly electricity-intensive process requiring between 3065 kWh/tonne and 3960 kWh ton$^{-1,}$ depending on the cell type [32]. In the process, an electric current is used to separate molecules into their constituents. The products of the process include chlorine and caustic soda. Table 3 exhibits estimated energy consumption for the various cell types.

**Table 3.** Energy consumption for $Cl_2$ production with mercury, diaphragm, and membrane cells.

| Component | Units | Mercury | Diaphragm | Membrane |
|---|---|---|---|---|
| Steam | GJ ton$^{-1}$ | 0.1 | 2.6 | 0.5 |
| Electricity | kWh ton$^{-1}$ | 3420 | 3140 | 2720 |
| Total – Primary Energy | GJ ton$^{-1}$Percent | 37.4 | 36.8 | 30.2 |
| Shares in U.S. (1994) | | 15% | 75% | 8% |

For further information, see the comprise the energy consumption of the chemical compounds in Table 4 [29, 31, 33].

As can be seen, a few chemical products dominate energy use, i.e., ethylene and co-products, ammonia, chlorine, and methanol.

**Table 4.** energy consumption for selected key chemicals.

| **Product** | **Estimated FinalEnergy SEC(GJ ton$^{-1}$)** | **Production(million tonnes)** | **Estimated TotalEnergy Use in (PJ)** | **Percent Share ofSIC 28 Energy Use (%)** |
|---|---|---|---|---|
| Ethylene and co-products | 67.5 | 26.2 | 1768 | 29.3% |
| Methanol | 38.4 | 4.9 | 188 | 3.1% |
| Polyethylene | 9.3 | 5.7 | 53 | 0.9% |
| Polypropylene | 10.5 | 4.4 | 45 | 0.7% |
| Polyvinyl Chloride | 11.6 | 5.4 | 62 | 1.0% |
| Polystyrene | 9.3 | 2.6 | 24 | 0.4% |
| Nitrogen | 1.8 | 28.6 | 49 | 0.8% |
| Oxygen | 1.8 | 22.7 | 44 | 0.7% |
| Ammonia | 39.8 | 16.2 | 645 | 10.5% |
| Urea | 2.8 | 7.6 | 21 | 0.3% |
| Chlorine | 19.2 | 11.1 | 213 | 3.5% |
| **Total** | **3112** | **51.5%** | | |

*1.5. Linkage between forests and plastic wastes.*

There is a pervasive effect of polymer pollution in both terrestrial and aquatic ecosystems. Polymers and resin waste that has come into contact with the forest environment cause complexity and is a health concern to all organisms. Polymers are being produced and stored in unbelievable amounts in forests, rivers, and other parts of the environment due to indiscriminate use, inadequate recycling, and accumulation on the land. Polymer waste currently poses a challenging subject for ecologists. Forest contamination is appearing at an incredible rate as polymer waste into terrestrial and aquatic ecosystems, which causes large challenges to managing waste for growing populations. The global spreading of the SARS-CoV-2 virus informed us of the endless COVID-19 [34-36] pandemic within the cutting-edge world accredited to the exploitation of the environment. Civilization is the main reason for being inhabited by bacteria and microorganisms due to polymer waste, and as a result, COVID-19 has attacked human habitations. Due to the outbreak of Coronavirus, manufacturers and producers of various polymers and resins have exponentially increased within the domestic segment of the lockdown due to the manufacturing and disposal of this exact shape. The onset of the COVID-19 pandemic has brought serious alarm to the devastating problem on human health, which has led to a carbon-positive setting, with increased amounts of greenhouse gases produced by dispensing waste plastics. Notably, plastic clinical wastes produced for coronavirus disease will continue to be discarded non-systematically within the post-COVID-19 era, posing an ecology-threatening polluting movement. In contrast to the important roles of forests in making livelihoods, they are being destroyed by several human activities like deforestation, unlawful logging, and poaching, amongst others. Deforestation has been verified to affect the lifestyles of flora and fauna species and ensure sustainability challenges. Polymers are widely used in society and are also environmentally sustainable when disposed of. Plastics degrade under different environmental conditions through four main mechanisms: photodegradation, thermal degradation, hydrolysis, and microbiological degradation. Through this study, we calculated the stability of polymers from the viewpoint of bio thermochemistry and investigated the relationship between energy use in Türkiye, including the economic advantages or disadvantages of producing these polymers.

### *1.6. Forests, wildlife, and plastic wastes.*

Sustainable forest management is related to the responsibility in the relevant environment in a way that does not harm economic and social outputs at different levels. Approximately 1 billion people apply fuelwood and coal as initial fuel for cooking and heating their life, which means the importance of forests in safeguarding survival altogether. Forests serve as primary sources of food components to complement products found in agriculture, as well as a source of raw materials for the food, pharmaceutical, wood, and furniture industries. Those have been provided with nutrient cycling in soil and water conservation. Plastic waste management is necessary for sustainable forest use, leading to the targets for recyclability and incorporating recycled plastics into products. Plastic pollution is caused in forests and wildlife by releasing some chemical compounds, such as Phthalate esters and Bisphenol compounds, into nutrition cycles which perturb the hormone systems of vertebrates and invertebrates (due to the release of substances that generate hormone imbalances). Plastic wastes cause numerous biological functions of animals, and with sustainable forestry practices, plastic waste can be reduced, which positively impacts the ecosystem. The spread of the SARS-CoV-2 virus oriented us to the dangerous COVID-19 pandemic [35,36] world and attacked the civilizations and most advanced countries due to the abnormal exploitation of the environment and massively killed its fatality, economy, and ecology. Seemly, urban life is restricted through bacteria and microorganisms that are building up their plastic waste, and easily, COVID-19 has invaded human habitations. Among the ignored factor of this poignant occasion has been the intensification in the quantity of plastic waste generated inside the shape of clinical waste, viz., face masks and pliable shields, analysis apparatus, PPE kits, medicinal syringes, etc. The problems of coronaviruses have brought serious subjects to human health, leading us to unusual carbon production because of large amounts of greenhouse gases produced by dispensing waste plastics. Recent research exhibited that the terrestrial hazard of plastic contaminants is grown time by time, particularly amidst the COVID-19 pandemic. Based on an approximation of the global plastic waste generation rate of 1.8 million tons per day from the inception of the COVID-19 pandemic, over 900 million tons of plastic waste were generated in 3 years of the pandemic [34-36]. Due to COVID-19, the economic, health, and social phenomenon of plastic waste manufacturing, construction, and treatment methods across the world have been changed completely (the reason being the usage of clinical-use plastic). Although using plastic in combating the COVID-19 pandemic stored hundreds of thousands of lives; however plastic clinical wastes will continue to be discarded non-systematically within the post-COVID-19 era, posing an ecology-threatening polluting movement. The negative effect of plastic pollution on agriculture or aquaculture creates new glitches in productivity and income generation opportunities. China is the principal consumer of plastic effluence in agricultural systems, and about 0.58 million tonnes of plastic have been mixed with the agricultural soil [37]. Therefore this plastic pollution affects not only soil health but also nutrition security and human health make a problem. Strangely, Plastic compounds have been discovered in human guts and feces [38-41]. However, Nano plasticity at high concentrations causes direct communication with RBCs leading to hemolysis [42]. Moreover, lanthanides and actinides are also absorbed on plastic surfaces, which is also dangerous to human health. Although plastic causes cancer in the gastrointestinal tract, stomach, and immune systems, little is known about the effects of trace-plastics-sorbent particulate plastic on humans. It is a necessity to find substitutes for biodegradable plastic waste instead of non-biodegradable plastics

## 2. Materials and Methods

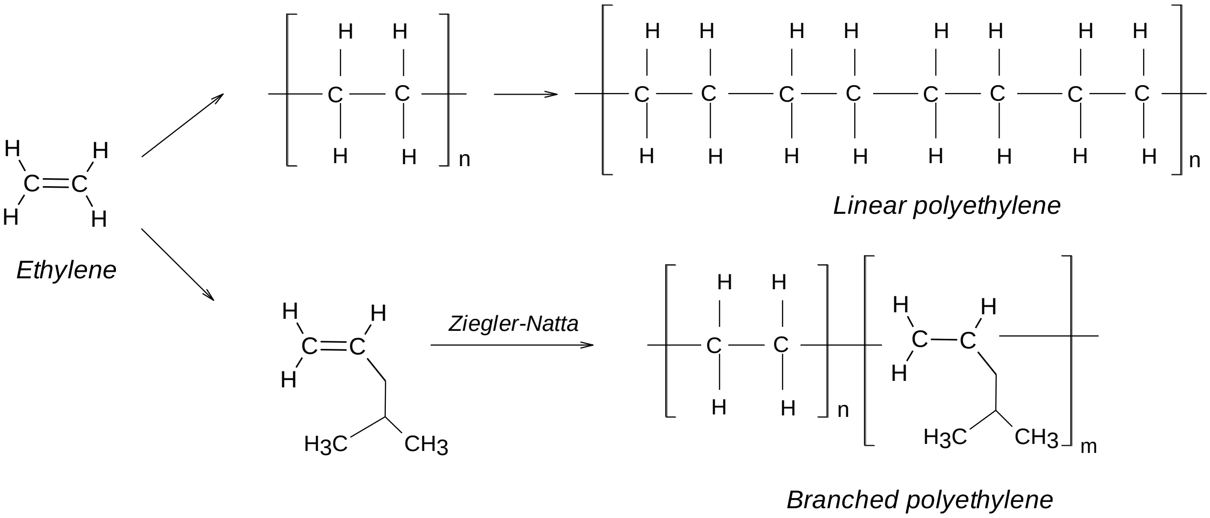
Petro-polymers like polyethylene (PE), polystyrene (PS), polypropylene (PP), polyvinyl chloride (PVC) and polyethylene terephthalate (PET), polyurethane (PU) are highly resistant to natural biodegradation. The structures of PE, PS, PP, and PVC plastics have a backbone made of C-C bonds. Polyhydroxyalkanoate (PHA) and polylactic acid (PLA) as biodegradable aliphatic polyesters have been made and might be employed as substituents for some of the petro-plastics compounds [43, 44]. Prokaryotic microorganisms can produce a group of polymers as polyhydroxyalkanoates (PHAs) for storing carbons [45]. PHAs have been selected with biodegradability in various conditions, chemical diversity, and biocompatibility, and they are produced from sustainable carbon sources and generated non-polluted compounds through the degradation step [44].

### *2.1. Polyethylene (PE).*

Some methods form polyethylene by adding ethene polymerization, which is fundamentally generated by breaking ethane and propane, naphtha, and gas oil. In fact, branched polyethylene is usually built by free radical vinyl polymerization, but linear polyethylene is formed with a more complex mechanism of the Ziegler-Natta method.

Branched polyethylene is usually built by free radical vinyl polymerization, but linear polyethylene is formed with a more complex mechanism of the Ziegler-Natta method (Scheme 2).

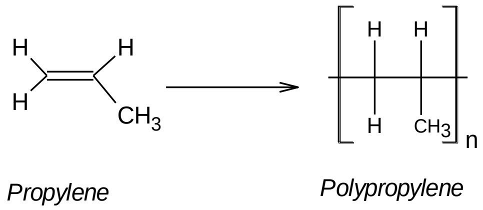
Thermochemical parameters indicate the amounts of the heat and free energies of polymerization of gaseous ethylene as a straight chain of PE molecules. The limiting values at 25°C for long-chain molecules of polyethylene are $\Delta H^{\circ}_{f}$ = -22.348 kcal/mol, with $n \geqq 3$ for the number of ethylene units per polymer molecule, and the value for the heat of combustion of solid polyethylene at 25°C, $\Delta H°_c = -311.8$ kcal $mol^{-1}$.




**Scheme 2.** The mechanism of polyethylene formation.

*2.2. Polypropylene (PP).*

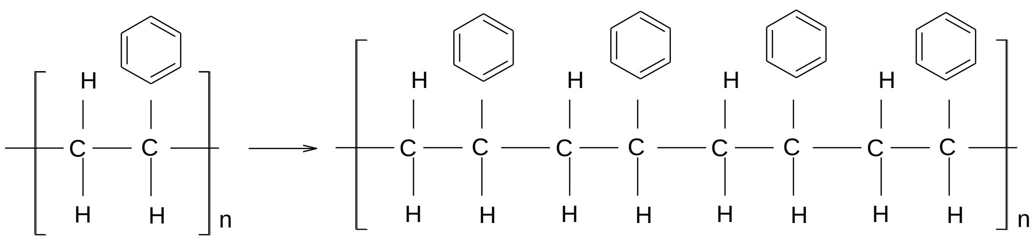
Polypropylene (PP), a thermoplastic polymer with many applications, is generated by the chain-growth method of polymerization from the monomer propylene molecule. This polymer is related to polyolefins with crystalline and non-polar structures. Its character is close to polyethylene but harder with more heat resistance [46] (Scheme 3).




PP is often close to PE (polyethylene), particularly in the liquid state and electronic characteristics. The methyl group develops mechanical parameters and thermal resistance. The PP properties are related to the molecular weight and its expansion, crystal properties, type, and the isotacticity that the methyl groups are directed on one side of the carbon chain, which this order generates a greater degree of crystallinity [47].

*2.3. Polystyrene (PS).*

Polystyrene is generated through an addition polymerization reaction from styrene monomers. The amount of the heat of reaction for this polymerization at 25°C is about -29 kcal $mol^{-1}$ which is an exothermic reaction.



Styrene → Polystrene  $\Delta H°_f = -28.95$ kcal $mol^{-1}$

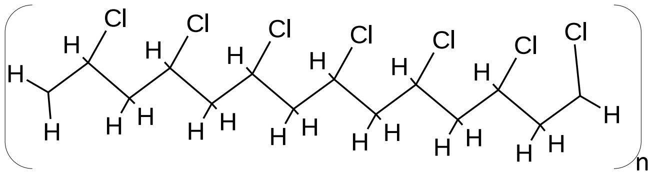
**Scheme 3.** The addition polymerization of styrene.

The addition polymerization of styrene starts through a free radical and initiator of di(dodecanoyl) peroxide due to the -O-O- group between two large groups of [$CH_3(CH_2)_{10}CO$-], which breaks easily to the free radical of [$CH_3(CH_2)_{10}CO.$)].

*2.4. PVC.*

While the monomer of vinyl chloride with $T_b$= 259K is a gas, under pressure and contraction will become liquid due to making the molecules closer together.

So, the polymerization reaction is done under a P= 13 atm and T= 325-350 K for maintaining the monomer in the liquid state, which is an exothermic reaction as follows (Scheme 4).

$CH_2 = CHCl \rightarrow$  $\rightarrow$ -[$CH_2$-CHCl]$_n$-

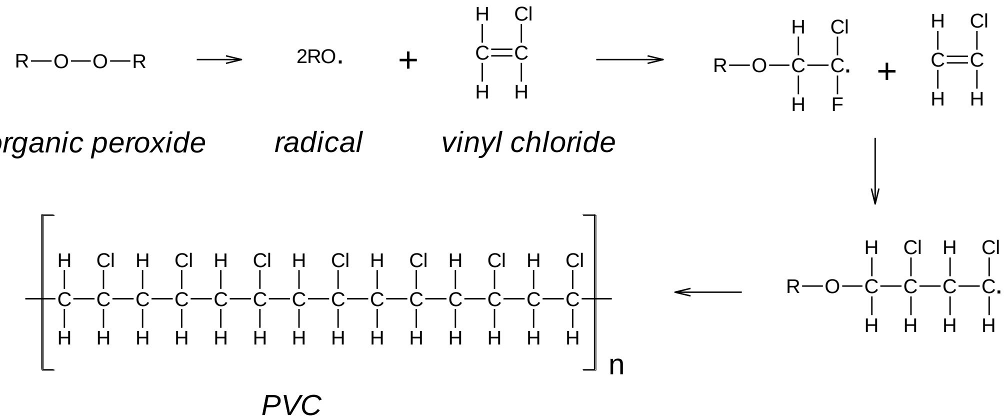


vinyl chloride polyvinyl chloride (PVC)

$\Delta H°_f$ = - 22.9665 kcal mol$^{-1}$

**Scheme 4.** Enthalpy energy of PVC product

The polymerization of chloroethene to form PVC proceeds by a free-radical mechanism with no charge and an unpaired valence. In the industrial preparation of PVC, a free radical is used to initiate the chain reaction as an R-O-O-R structure which is converted to free radicals at high temperature, then reacted with vinyl chloride to produce another radical. In the next step, the new free radical is able to join with another vinyl chloride. Finally, this new free radical again reacts with vinyl chloride to form a new free radical until a huge polyvinyl chloride (PVC) has been produced and polymerization will finish (Scheme 5).





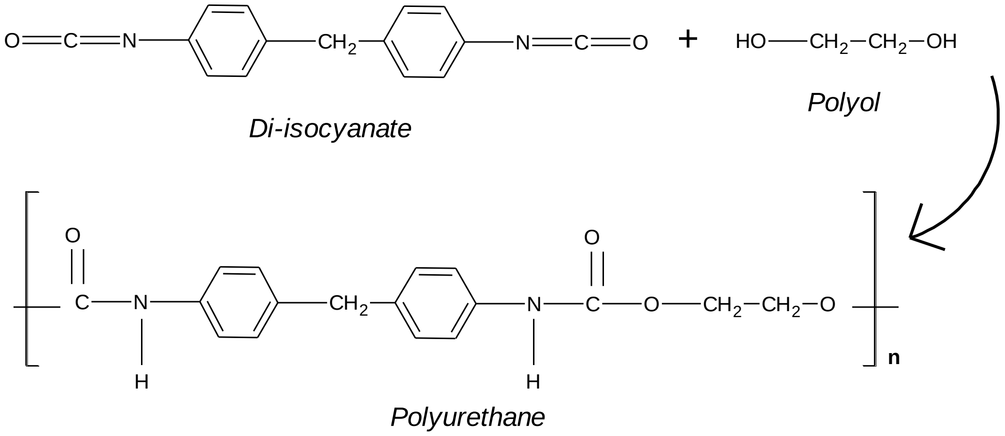
**Scheme 5.** Mechanism of polyvinyl chloride (PVC).

*2.6. Polyurethane (PU).*

PUs are often generated from the chemical reaction of polyol and isocyanate molecules in the presence of light and enzymes (Scheme 6). Polyols and isocyanates derived from PU consist of many factors which cause them to be necessary for local and industrial goals.

It has been approved that PUs are chemically inactive and may include containing dangerous compounds such as amines, glycols, and phosphate, which are probably hazardous to the skin systems, respiratory tract, and the environment.

In industry, polyurethane foams are able to be employed as the appropriate adsorbents keeping the chemical compounds. The separation of chemical materials from water is an important environmental and industrial issue. The usage of the adsorption methodology has been considered a notable significance in the treatment of aqueous medium and swages.




$C_3H_7NO_2$ Urethane , $\Delta H°_{f}$ = -92.98 kcal mol

**Scheme 6.** The mechanism of producing polyurethanes.

Finally, the comparison of heat formation, heat capacity, and entropy for polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and nitrogen, oxygen, ammonia, and urea at 298.15K have been observed (Figure 2).

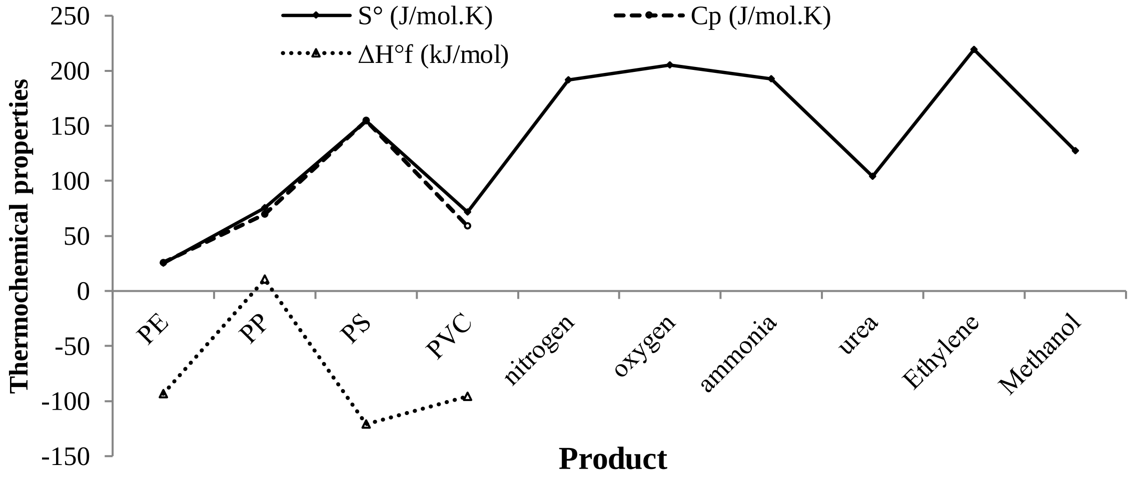
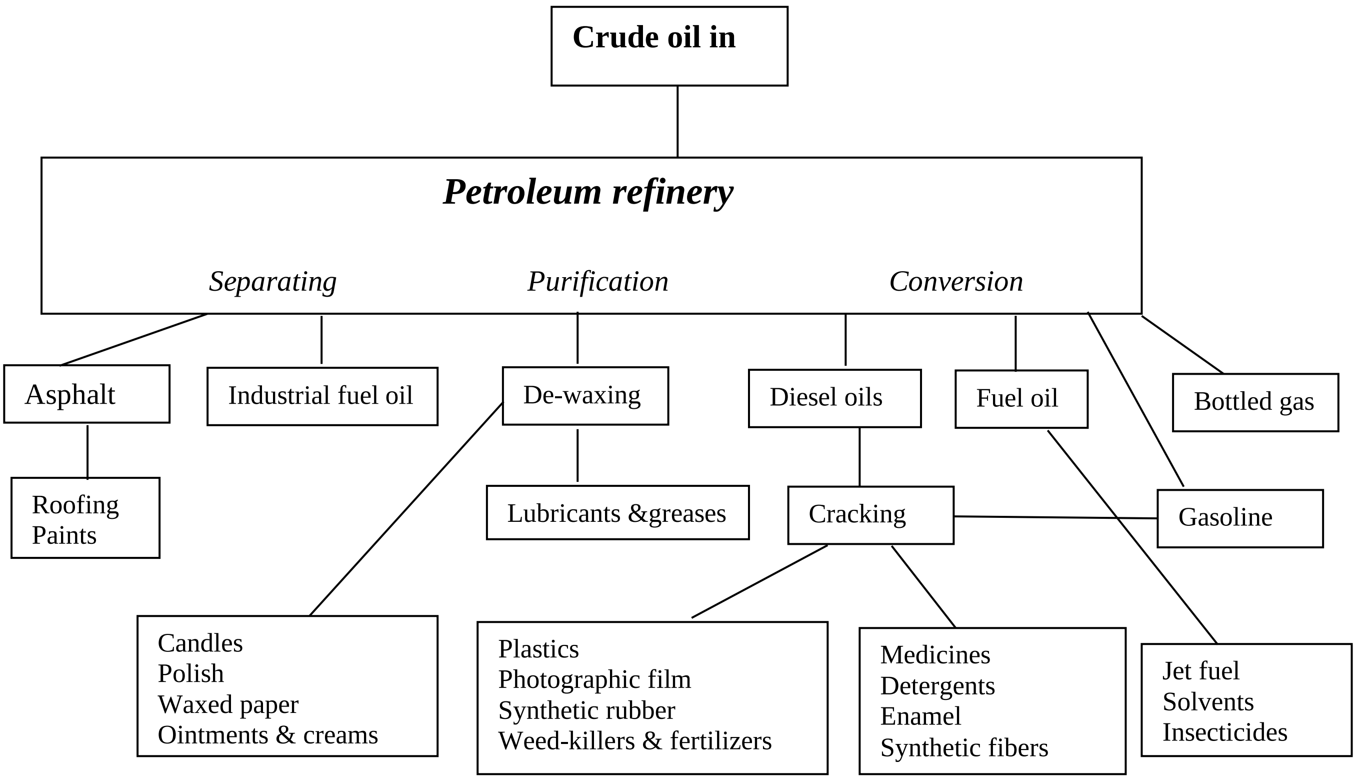



**Figure 2.** Comparison of thermochemical properties for the polymers; polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), nitrogen, oxygen, ammonia, and urea at 298.15K.

## 3. Results and Discussion

### *3.1. Industry of petrochemical*

These results reflect an in-depth analysis of a part of petrochemical as one of the energy-intensive sub-sectors. Most simple molecular organics such as ethylene, propylene, and benzene are prepared in petrochemical factories. These products form the root of many materials, such as resins, fibers, detergents, and plastics. The only most energy-consuming section in petrochemical processing is the steam cracking of hydrocarbon for providing $C_2H_4$, $C_3H_6$, $C_4H_8$ (butadiene), and $C_6H_6$ or $C_7H_8$ (toluene). Up to now, an exact evaluation of world energy consumption for $C_2H_4$ and co-materials are not registered. However, in the past three decades, (1990) energy consumption was evaluated to be about around 950 TBtu (excluding feedstock energy consumption), with $C_2H_4$ materials amounting to fifty Million tonnes[1]. In a cracking phenomenon, mostly alkane products are heated up to 700°C, then mixed and cracked at a temperature of around 900°C [30]. In further processing, the mixture is quickly cooled to 350°C to stop the reaction, during which high-pressure steam is produced. Diffusion of water decreases the temperature to about 45-55°C, and a condensate, rich in benzene, naphthalene, anthracene, phenanthrene, and several other aromatic compounds, is formed. The liquid segment can be extracted, while the gaseous section is fed to a series of low-temperature, high-pressure distillation columns [46]. The initial products are $C_2H_6$, LPG, naphtha, and gas oils. If $C_2H_6$ is used as feedstock, consequently, $C_3H_6$, $C_4H_8$, and aromatic compounds cannot be formed. Therefore, other processes are used for producing these chemicals in countries that predominantly use ethane cracking. Another item is catalytic cracking for the dehydrogenation of $C_3H_8$, which is not used all time.




**Scheme 7.** Heating & catalytic cracking steps

**Table 5.** Influence of feedstock on steam cracker yield.

| **Product** | **Feedstock** | | | | | |
|---|---|---|---|---|---|---|
| | **Ethane** | **Propane** | **Butane** | **Naphtha** | **Atmospheric gas oil** | **Vacuum gas oil** |
| **Hydrogen (95% purity)** | 9 | 2 | 2 | 2 | 1 | 1 |
| **Methane** | 6 | 28 | 22 | 17 | 11 | 9 |
| **Ethylene** | 78 | 42 | 40 | 34 | 26 | 21 |
| **Propylene** | 3 | 17 | 17 | 16 | 16 | 14 |
| **Butadiene** | 2 | 3 | 4 | 5 | 5 | 5 |
| **Pyrolysis gasoline Of which:** | 2 | 7 | 7 | 19 | 18 | 19 |
| - **Benzene** | 2 | 3 | 3 | 7 | 6 | 4 |
| - **Toluene** | 0 | 1 | 1 | 3 | 3 | 3 |

$C_6H_6$, $C_7H_8$ (toluene), and xylenes are usually produced through hydrogenation and desulphurization of pyrolysis gasoline, after which the different components are separated by solvent/solvent extraction. Table 7 shows how product yield varies with feedstock type[47] (Scheme 7).

Due to the emphasis on ethylene compound as the most used industrial molecule from steam cracking, the unit energy consumption $C_2H_4$/tonne, known by SECe abbreviation, is a popular measure of energy consumption for cracking. This item (SECe) in a modern factory is 14 GJ/tonne for $C_2H_4/C_2H_6$ cracking and 20-27 GJ/tonne for $C_2H_6$/ naphtha cracking.

The production steps in the ethylene reactor can be seen in Scheme 8. In total, fuels are used to fire the cracking furnace and to produce steam to drive compressors and pumps with for produce steam to drive compressors and pump with dilution steam generation and low-pressure steam for direct process heating [48]. Due to the lower ethylene yield in the final process, higher feed volumes are required to prepare the same amount of ethylene as ethane. The calculation is shown in the data in Table 6 exhibits how energy consumption varies with feedstock [49].

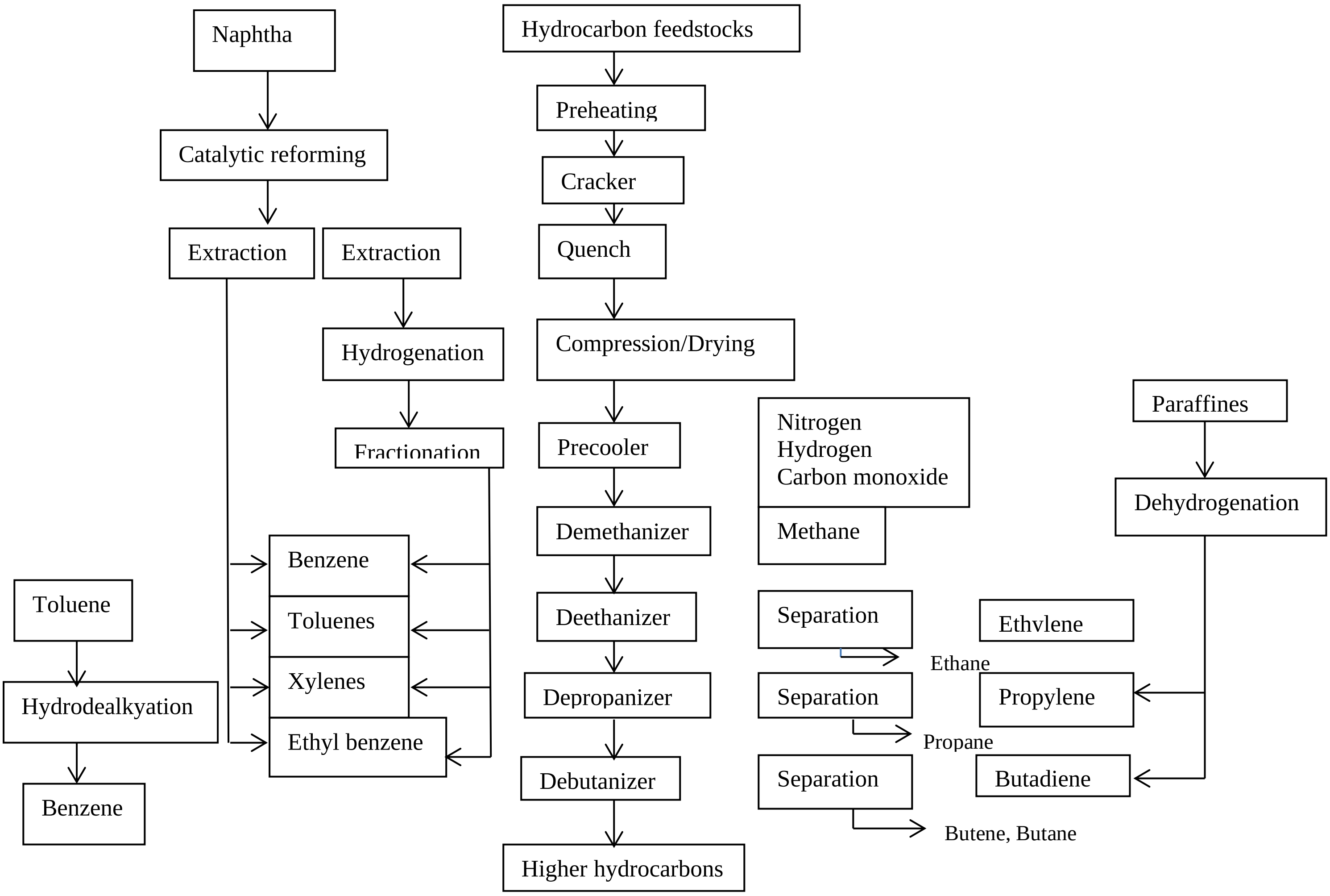
**Table 6.** Breakdown of primary specific energy consumption.

| | Feedstock | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ethane | | Naphtha | | Gas oil | | U.S. Mix | |
| | GJ/t | % | GJ/t | % | GJ/t | % | GJ/t | % |
| Heat of reaction | 4.8 | 21 | 6.2 | 20 | 12.4 | 33 | 6.0 | 23 |
| Compression | 3.5 | 16 | 3.5 | 13 | 4.1 | 11 | 3.7 | 14 |
| Heating & separation losses | 14.2 | 63 | 17.7 | 66 | 20.6 | 55 | 16.8 | 63 |
| SEC | 19.4 | | 26.2 | | 31.9 | | 26.5 | |

*3.2. Industry of ammonia and nitrogen fertilizer.*

The nitrogen fertilizer industry is a huge energy consumer, especially since the production of ammonia is the most one in the manufacture of fertilizers. In Türkiye, most of the ammonia is used for fertilizer production. The most important fertilizers produced are nitrate, $HNO_3$, urea, compound fertilizers, and liquid ammonia. $NH_4SO_4$ is the most generally produced as a co-product of nylon manufacturing. $NH_3$ is produced by the reaction of $N_2$ and $H_2$, based on the Haber process. The $H_2$ production processes used in the U.S. are steam reforming natural gas and partial oxidation of oil residues. $H_2$ is produced by reforming the hydrocarbon feedstock, producing a synthesis gas of carbon monoxide and $H_2$. The CO is then reacted with steam in the water-gas-shift reaction to produce CO and $H_2$. The $CO_2$ is removed from the main gas stream.

The $CO_2$ is recovered for urea production or exported as a co-product or vented. The $H_2$ reacts with $N_2$ in the final synthesis loop to form $NH_3$ [50,51]. Although $NH_3$ is used directly as a fertilizer, most of the $NH_3$ is converted to other compounds to be used as fertilizer. We give a short description of the main processes for fertilizer production. Urea is produced in two steps by the reaction of $NH_3$ and $CO_2$. The $CO_2$ is produced in the $NH_3$ synthesis. In the first step, carbamate ($NH_2CO_2NH_4$) is synthesized. In the second step, the carbamate is dehydrated to $CO(NH_2)_2$ (urea). The reaction is not complete. Therefore $NH_3$ and $CO_2$ are both stripped from the urea solution and recycled. Nitric Acid is used mainly to produce ammonium nitrate ($NH_4NO_3$). $HNO_3$ is also used to produce non-fertilizer products. $NH_3$ is burned over catalysts to produce nitrous oxides. The total process is highly exothermic, so waste heat boilers are installed to generate superheated high-pressure steam. The neutralization of $HNO_3$ with $NH_3$ in an exothermic reaction produces $NH_4NO_3$. The released heat can be used in the process internally and can produce steam, which can be exported.



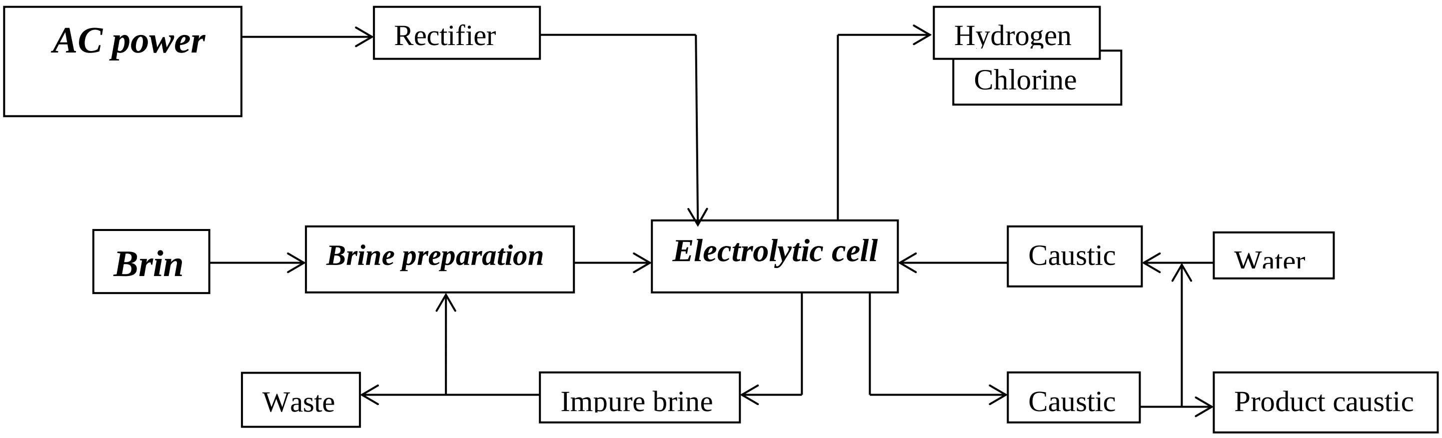

**Scheme 8.** Process routes for the production of ethylene and its co-products [8].

Older plants work at atmospheric pressures, but most modern processes work at elevated pressures. $(NH_4)_2SO_4$ is produced as a byproduct of nylon. In the synthesis of caprolactam, ammonia is added to control the reaction. As much as three to five times as much ammonium sulfate may be produced than caprolactam. Notably, energy consumption for ammonia and fertilizer production consists of consumption as energy for fueling the chemical process, as well as the energy used as feedstock, and based on molecular stoichiometry, 20% of the $CO(NH_2)_2$ is carbon which means huge $CO_2$ can be produced from $CO(NH_2)_2$.

*3.3. Industry of chlorine.*

Chlorine and alkaline production are closely connected due to the feedstock used (salt). This sub-sector is one of the most energy and electricity-intensive industries. The major markets for chlorine are PVC, inorganic chemicals, other organic chemicals, propylene oxide, pulp and paper, and water treatment or solvents. The major markets for caustic are pulp and paper, soaps and detergents, propylene oxide, petroleum, water treatment, other organic chemicals, and inorganic chemicals. These areas are expected to continue to grow but below the historical rate of growth.

In part, the slower growth is attributable to the collapse of the Asian economies and to environmental concerns about the use of chlorine in industrial processes [51-53]. The production of chlorine gas is an energy-intensive chemical process requiring between 25-40 GJ (worldwide average) of primary energy per tonne of chlorine produced [8]. A brine solution is converted into two co-products through electrolysis: chlorine gas and sodium hydroxide (caustic soda). The mercury flow, diaphragm, or ion-selective membrane are the three main electrolysis cell types that separate and produce chlorine and caustic gas. The membrane cell requires the least energy to operate on the three cell types and is currently considered the state-of-the-art technology. Scheme 9 exhibits the main process stages for chlorine production.




**Scheme 9**. Simplified chlorine production flow chart.

## 4. Conclusions

The current report provides a detailed baseline of energy use from chemical fuels and using polymer compounds based on a biotermochemical assessment of the industrial products and technologies. This paper also analyzes the energy used in several kinds of production and unit operations for each step's energy intensity estimates. In addition, the problem of materials and industrial waste products due to climate change destroying forests has been discussed from the viewpoint of thermochemical processes.

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## Conflicts of Interest

The authors declare no conflict of interest.

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