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REVIEWS

Pathways of Chemical Recycling of Polyvinyl Chloride: Part 1

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Abstract—An increase in the level of production and consumption of polyvinyl chloride leads to the formation of a large volume of chlorinated waste, mostly as a component of municipal plastics waste. Incineration of such waste to produce energy results in emission of toxic gases (SO_2, NO_x) and of heavy metals and solid particles with flue gases, and also in formation of polychlorinated dibenzodioxins and dibenzofurans and of other aggressive chlorinated organic compounds. Therefore, recycling of waste containing chlorinated organic polymers becomes a serious problem. The review considers modern commercial processes for sorting municipal plastics waste, including various procedures for polymer waste separation. Procedures based on pyrolysis and gasification for chlorinated waste recycling are analyzed. Approaches to chemical recycling of polyvinyl chloride and of polymer mixtures and municipal waste containing polyvinyl chloride, namely, pyrolysis and low-temperature catalytic dechlorination, are described. The influence of the composition and kind of polymer waste on the degree of dechlorination is analyzed. Principles and mechanisms of mechanochemical processing of polyvinyl chloride waste in a mixture with chemical sorbents and with biological and technical wastes are presented.

Keywords: polyvinyl chloride, polyvinyl chloride waste, municipal plastics waste, dechlorination, pyrolysis, biomass, mechanochemical treatment

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INTRODUCTION

Improvement of commercially used and introduction of new methods for chemical recycling of polymer waste into monomers or chemical feedstock for the production of fuels and materials is a topical line in chemical technology [1, 2]. A significant problem that arises when using unsorted waste as a feedstock is the presence of halogenated compounds and polymers, especially if compounds recovered from secondary resources are involved in traditional processes of oil refining and petrochemistry, because even a minor impurity of halogenated compounds leads to poisoning of catalysts and damage of the equipment, so that it becomes necessary to take special corrosion prevention measures.

The major component of halogenated polymer waste is polyvinyl chloride. There are three types of polyvinyl chloride: pure, rigid, and flexible, depending on the presence/absence of certain additives [3]. The pure polymer, as a rule, contains 51–58 wt % chlorine. Polyvinyl chloride has a linear head-to-tail structure. Typical number-average molecular masses are 50 000–120 000 g mol^{-1}. Pure polyvinyl chloride resin is hard and strong, but it is of virtually no use in practice because of unsatisfactory resistance to high temperatures and UV radiation. Addition of stabilizers such as heavy metal (barium, tin, cadmium, lead) compounds considerably enhances the polymer resistance to heat and light. The chlorine content of rigid polyvinyl chloride does not exceed 45–48% [4], because the fraction of pure polyvinyl chloride in this material does not exceed 90%. Such polymer is used for the production of pipes, air pipelines, building panels, floor covers, and other items for building. Increased flexibility required for use in films, pipes, wire insulation, etc., is imparted to polyvinyl chloride resin by its blending with various plasticizers, usually with organic esters (di-2-ethylhexyl phthalate, dioctyl phthalate). In flexible polyvinyl chloride, the chlorine content is considerably lower (22–

35%) [4]. Addition of bromine, antimony, or phosphorus compounds makes the product flame-resistant.

In 2013, the polyvinyl chloride production volume was about 61 mln tons [5], of which more than a half (38.5 mln tons) was produced in China. It is expected that, by 2023, the polyvinyl chloride production capacity will reach 63.7 mln tons at the demand of 51.6 mln tons. The main polyvinyl chloride producers are Asian (48%) and North American (13%) countries. Asian countries are also the main consumers (58%); the share of European countries in the total consumption is 17%. In Russia, the polyvinyl production and consumption volume in 2019 was about 1 mln tons.

The commercial significance of polyvinyl chloride predetermines the importance of solving the problem of joint chemical recycling of polymer waste [5] containing, as a rule, a mixture of polyvinyl chloride with polyethylene, polypropylene, polystyrene, poly(ethylene terephthalate), etc. [6]. Hydrogen chloride released in the course of thermal degradation of polyvinyl chloride causes the equipment corrosion [5]; in the process, hydrogen chloride can react with monomers and cyclic compounds formed in the course of polyvinyl chloride decomposition to form chlorinated organic by-products. Combustion and disposal of polymer waste causes significant damage to the environment. Mechanical recycling of solid municipal waste containing chlorinated plastics is complicated by the presence of food, building, and other wastes as impurities and by the waste heterogeneity.

Owing to the use of advanced technologies for polymer waste recycling by depolymerization to polymers of lower molecular mass or to monomers (pyrolysis) or by partial degradation to valuable secondary materials (chemical depolymerization), chemical recycling (so-called tertiary recycling) becomes more and more topical.

In this review, we analyze the literature and patent information in the field of recycling chlorinated polymer waste with the aim to reveal the main trends in the development of dechlorination technologies, to analyze the dechlorination mechanism in various processes, to generalize the industrial experience in recycling chlorinated plastics, and to evaluate prospects for producing monomers from chlorinated macromolecular compounds. The first part of the review deals with the modern commercial procedures for sorting municipal plastics waste (i.e., for primary recycling) and for chlorinated waste recycling: mechanochemical (secondary) and chemical (tertiary), including pyrolysis and low-temperature catalytic dechlorination.

INDUSTRIAL EXPERIENCE IN RECYCLING CHLORINATED POLYMER WASTE

Waste consisting of polyvinyl chloride and polyvinylidene chloride (so-called postindustrial waste [2]) without any impurities is formed only at specialized enterprises as cut pieces, turnings, etc. This waste can be delivered to secondary recycling without any pretreatment [7].

Municipal plastic waste consists, as a rule, of mixed plastic potentially contaminated with food residues, paper, cardboard, and other organic or inorganic substances [8], which complicates further recycling. Usually plastics waste is a mixture of polypropylene, polystyrene, polyethylene, polyvinyl chloride, acrylonitrile–butadiene–styrene copolymer, polyvinylidene chloride, poly(ethylene terephthalate), etc.

The most widely used procedure for processing plastics waste, including chlorinated polymers, is mechanical recycling [9, 10]. Its steps are collecting, sorting, washing, and finely dividing the material. Only in 2015, of 25 mln tons of plastics waste in Europe,[1] 29.7 wt % was reprocessed, 39.5 wt % was converted to energy, and the remainder was disposed of.

Kikuchi et al. [11] suggested a two-step recycling procedure with which they were able to increase the fraction of plastics with low content of chlorinated components (from 13 to 47.5%), which can be utilized by combustion, and decrease the content of polyvinyl chloride rich plastics (from 52 to 16.9%) to be disposed of (Fig. 1). Polyvinyl chloride waste was reprocessed in a mixture with nonutilizable polymers whose fraction in the waste was 50–85 wt %.

The waste separation and sorting are based on the density, size, color, and chemical composition of the polymers. The sorted poly(ethylene terephthalate) and polyethylene wastes are delivered to secondary recycling. This is followed by washing to remove organic and food wastes and by cutting to flakes of 1–12 mm size, which are again washed. The second step

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[1] PlasticEurope, 2015, Plastics the Facts 2014/2015: an Analysis of European Plastics Production. Demand and Waste Data, PlasticEurope Brussels, Belgium. https://www.plasticseurope.org/en

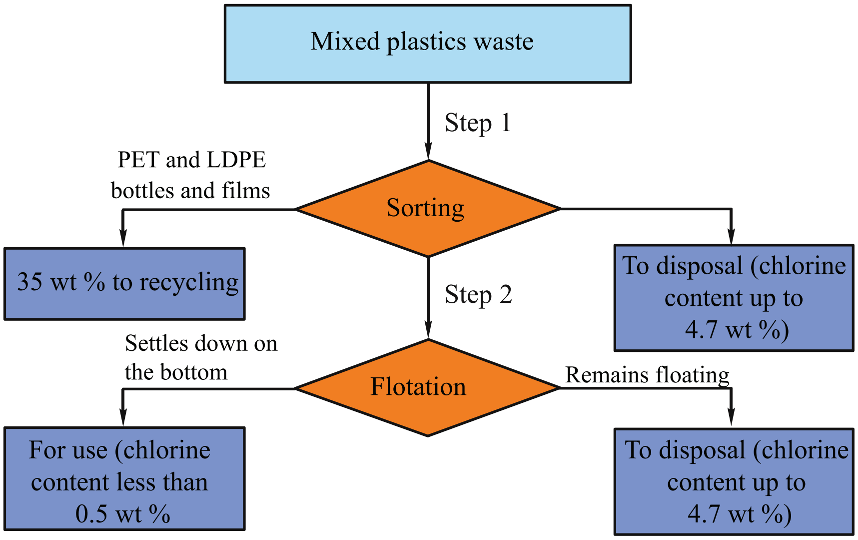

Fig. 1. (Color online) Two-step recycling of mixed plastics waste (adapted from [11]).

of the separation is flotation; this process is determined by the density of the polymers [12]. Polypropylene and polyethylene float up to the water surface when heated on a water bath, whereas other polymers whose density is higher than 1 g cm^{-3}, such as poly(ethylene terephthalate), polystyrene, acrylonitrile–butadiene–styrene copolymer, and polyvinyl chloride, on the contrary, sink. After drying, soft polypropylene and polyethylene wastes are subjected to final regranulation (with filtration from melt) and subsequent use as a secondary raw material.

In electrostatic separation, the collision of polymer flakes with each other results in the formation of a positive charge on the surface of one of the polymers and negative charge on the surface of the other polymer [9]. Binary mixtures of polystyrene, polyvinyl chloride, poly(ethylene terephthalate), and polyamide can be separated by such procedure [12]. Polymers with equal densities are separated by foam flotation based on the differences in the wettability of the polymer surfaces [13]. Owing to low surface tension, hydrophobic polymers become concentrated at the air–water interface and do not sink because of interaction with air bubbles, whereas polymers that are well wetted with water sink to the bottom. Polyvinyl chloride is mostly hydrophobic and is thus separated from polar polymers (Fig. 1). As a rule, polyvinyl chloride as the only chlorinated polymer in the mixture is detected by X-ray fluorescence analysis.

The major problems associated with the mechanical recycling consist in the polymer degradation under the action of thermomechanical treatment, heat, oxidation, light, ionic irradiation, hydrolysis, etc., deteriorating the physicochemical properties of polymers for further recycling and use [14].

The difference in the melting points and, as a consequence, in the polymer treatment temperature in mixed plastics gives rise to additional problems in recycling mixed plastics. The recycling is often performed at the temperature required for treatment of the higher-melting polymer present in the mixture, which leads to overheating and degradation of some lower-melting components and thus to deterioration of their properties. This is particularly topical for mixtures containing polyvinyl chloride and poly(ethylene terephthalate) whose reprocessing is performed at elevated temperatures; in the process, poly(ethylene terephthalate) considerably accelerates the polyvinyl chloride dehydrochlorination [6].

The mechanochemical recycling in which chlorinated polymers are milled with filler or sorbents allows preparation of a solid residue that can be used in building as an alternative to asphalt (for road paving etc.) and as synthetic fuel if its calorific value exceeds 30–35 MJ kg^{-1}.

Because combustion of chlorinated waste leads to the formation of toxic polychlorinated dibenzodioxins,

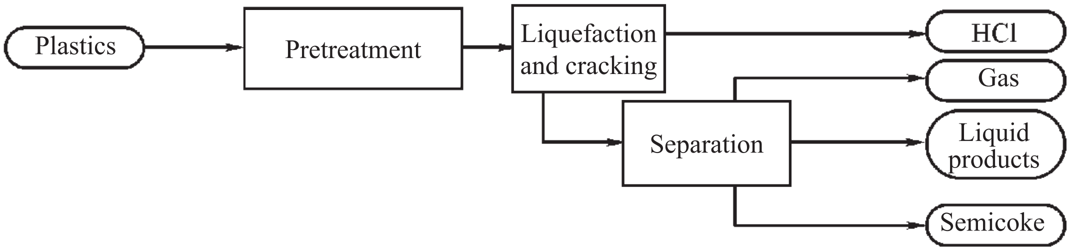

Fig. 2. Scheme of the BASF process (adapted from [19]).

dibenzofurans, and other chlorinated organic compounds, the combustion of hazardous waste in some countries is subject to regulations. For example, in Finland the reclaimed or synthetic fuel is subdivided into three types with respect to the content of chlorinated compounds: type I, chlorine content lower than 0.15%; type II, lower than 0.5%; and type III, lower than 1.5%; combustion of only feedstock of types I and II is allowed.[2] Even at low chlorine content of waste, chlorinated compounds are formed in light ash [15]. For example, in combustion of a biomass containing ~0.5 wt % Cl, the chlorine content of the ash will reach up to 10 wt %, and in combustion of solid waste it will range from 1.8 to 9.1 wt % [16].

The presence of coatings and paints on polymer waste considerably complicates the mechanical recycling. The contaminating substances can be incompletely soluble and can cause the phase segregation with negative effect on the mechanical properties of the polymer [9].

The main method of chemical recycling is pyrolysis of mixed polymers to obtain, as a rule, monomers and petrochemical feedstock, which can be subsequently used for producing various products. The presence of even small amounts of chlorinated compounds in pyrolysis oil or waxes does not allow pyrolysis products to be used as a fuel or petrochemical feedstock; the content of chlorinated compounds in liquid products should not exceed 10 ppm [6]. Therefore, the pyrolysis is performed either at decreased temperatures [6] or in the presence of sorbents at the beginning or end (in the case of two-step pyrolysis [17]) of the process, with the subsequent removal of chlorides from wastewater by precipitation using $CaCO_3$, CaO, $NaHCO_3$, Na_2CO_3, or NH_3. The pyrolysis oil thus obtained is used in catalytic cracking for the production of gasoline or directly as black oil. The chlorine content of municipal plastics waste can also be decreased by dechlorination initiated by microwave radiation at relatively low temperatures [18].

The main pyrolysis technology is the BASF technology (Fig. 2) [19] implemented for the first time on an installation with an annual capacity of 15 000 t (Badische Anilin und Soda Fabrik, Ludwigshafen, Germany) in 1994. The waste recycling starts with the pretreatment. In this step, mixed plastics are finely divided and separated from metals and agglomerated materials. In the next step, the polymer waste is melted and dehalogenated to protect the equipment segments from corrosion. The major fraction of chlorine released in the form of HCl is absorbed and used in the production of hydrochloric acid, and a minor fraction of chlorine is removed in the form of NaCl and $CaCl_2$ through wastewater. Gaseous organic products are liquefied and used as a cracker feedstock. In the next steps, the liquefied plastics waste is heated to 400°C; in so doing, it degrades to form components of different chain lengths. The process yields approximately 20–30% gases and 60–70% oils, which are subsequently separated in a distillation column. The naphtha is treated in a steam cracking installation, and the monomers (ethylene, propylene) are reduced. High-boiling oils can be processed to obtain syngas or semicoke for the subsequent use.

The pyrolytic Akzo process (Netherlands), which is efficiently used for recycling of polyvinyl chloride rich plastics waste with the productive capacity of 30 kg h^{-1}, is based on a system with circulating fluidized bed (two reactors) followed by combustion; the major products are HCl, CO, H_2, CH_4, and, depending on the feed composition, other hydrocarbons and light ash [20, 21].

The NRC process [9] is based on pyrolysis of polyvinyl chloride waste (cables, finishing materials for

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[2] VNp 1049/99 kaatopaikoista annetun valtioneuvoston päätöksen muuttamiseksi, 1999. https://finlex.fi/fi/laki/ajantasa/kumotut/1997/19970861

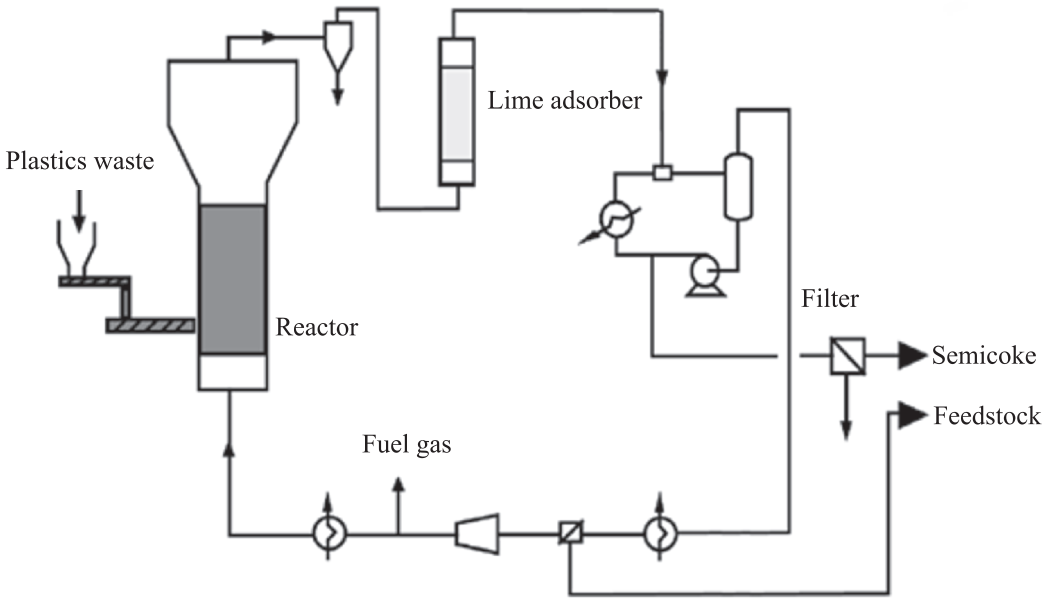

Fig. 3. Scheme of the BP polymer cracking process [20].[3]

building, profiles, etc.) using calcium sorbents, followed the recovery of heavy metals. The pyrolysis yields $CaCl_2$, coke, organic condensate (for use as a fuel), and the corresponding heavy metals.

Putting pilot installations (1994–1998) for BP polymer cracking process [20] (Fig. 3) into operation allowed setting up a plant with the annual productive capacity of 25 000 t in Scotland. Polymer waste with 2–4% polyvinyl chloride content, divided to a particle size of 1–20 mm, is fed under anaerobic conditions into the heated fluidized bed of the reactor (500°C). The hydrocarbons formed in the course of the polymer cracking are removed with the gas fluidizing the bed. The HCl released in the course of polyvinyl chloride degradation is neutralized with a solid lime absorbent. The process yields 5–8 wt % (based on the plastic weight) pyrolysis liquid, 15 wt % gases containing monomers (ethylene, propylene) and up to 15% methane [22], and 0.2 kg kg^{-1} semicoke (based on the total amount of dry matter).

An alternative technology for recycling municipal plastics waste (MPW) (especially polyvinyl chloride cable waste) is the NKT process (Fig. 4) [20, 21]. Its advantage is that the products contain no dioxins, chlorinated organic compounds, metals, and plasticizers. The process starts with the pretreatment to remove light plastics (polypropylene, polyethylene, etc.) and other contaminants (wood, sand, iron, steel, brass, copper, etc.). The municipal plastics waste is then fed to a reactor at low pressure (2–3 bar) and moderate temperature (375°C). A small amount of carbon dioxide formed by the reaction of lime with hydrogen chloride is released in the process.

The two-step pyrolysis of polyvinyl chloride waste with $CaCO_3$ as filler and sorbent in the NKT-Watech process at elevated temperatures leads to the break of polymer chains and formation of a large amount of semicoke. The calcium chloride formed in the process is treated for the subsequent use [23]. Catalytic cracking of waste containing polyvinyl chloride seems to be unfeasible because of rapid deactivation of the catalyst with Cl- or N-containing carbonaceous deposits formed in the process [24].

The process for catalytic pyrolysis at atmospheric pressure (Katalytische Drucklose Verölung) [25], developed by Alphakat GmbH, allows the production of diesel fuel, kerosene, and petroleum by catalytic conversion of biomass and mixed waste at atmospheric pressure with complete removal of oxygen, nitrogen, and chlorine atoms from the substrates (250–320°C). Dechlorination is performed by neutralization of the ion-exchange catalyst [23, 26].

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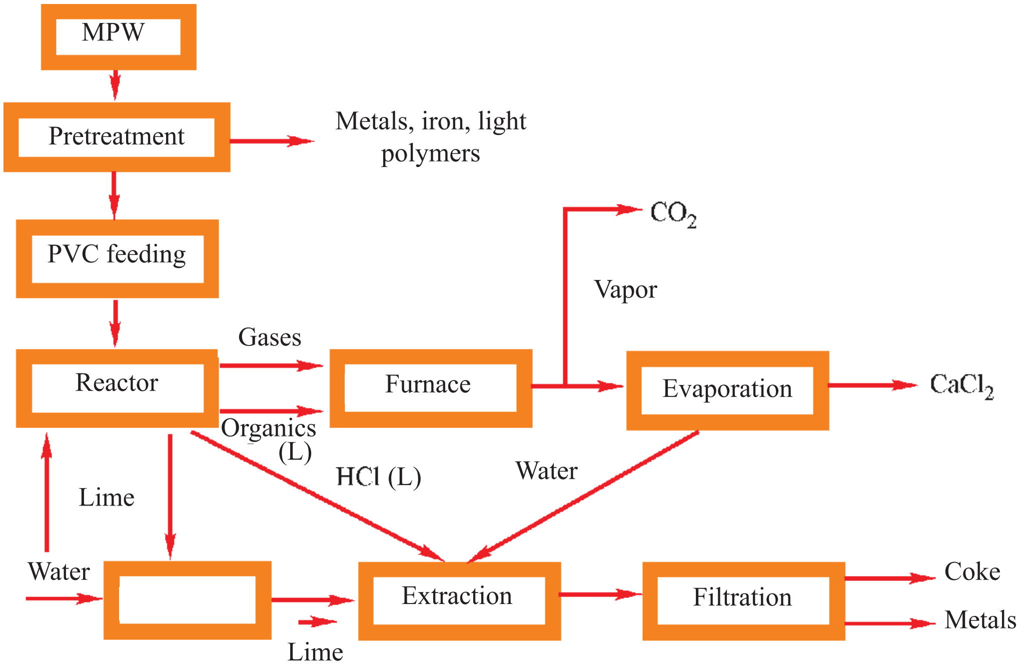

Fig. 4. (Color online) Scheme of the NKT process [20, 21].[4]

The Texaco plastics waste gasification process is today the most widely used processes among gasification procedures. The first pilot installations (10 t daily) were trialed in the United States [27]. Thermal liquefaction of municipal plastics waste containing up to 10% polyvinyl chloride results in depolymerization to obtain synthetic heavy oil and condensable and noncondensable gas fractions [28]. Gasification is performed with oxygen and steam at 1200–1500°C. After a series of purification processes (removal of HCl and HF), pure and dry syngas is obtained; it consists mainly of CO and H_2 with minor amounts of CH_4, CO_2, H_2O, and some inert gases [20]. The wastes are fed to the reactor (furnace) together with lignite (in the form of briquettes) and spent oil. Liquid hydrocarbons are subjected to further processing under oil pressure. The gas is mainly used for producing methanol and electric power.

One more commercial procedure for recycling chlorinated plastics waste is the Veba Combi cracking process (Veba Oel AG) based on hydrocracking, i.e., on the waste treatment with hydrogen (1992) [20, 21, 29]. In accordance with the Veba Oel AG technology, coal liquefaction yields naphtha and gas oil. The Veba Combi cracking process installation for recycling municipal plastics waste containing less than 4% polyvinyl chloride (62 wt % chlorine) consists of the depolymerization and hydrocracking sections. The polyvinyl chloride dechlorination and polymer waste degradation occur in the first section at 350–400°C. The major fraction of chlorine (80%) removed from polyvinyl chloride is HCl gas; its washing yields technical-grade hydrogen chloride. The partially condensed depolymerization product containing 18% hydrogen chloride [20] is introduced into the hydrotreating section in which HCl is removed with stratal water. The condensate treated to remove hydrogel chloride and the released gases is mixed with the depolymerized material for treatment in the hydrocracking section [30] and subjected to hydrogenation at 400–450°C under high pressure (≈100 bar) in a fixed-bed liquid-phase reactor. The hydrotreating product is separated to obtain synthetic crude oil and hydrogenating bitumen, a stream of hydrogenated residue containing heavy hydrocarbons contaminated with ash, metals, and inert salts. Mixing of this bitumen with coal allows production of coke (up to 2 wt %). The outlet gas (E-gas) contains light products capable of cracking; they are treated to remove H_2S and NH_3. The remaining fraction of chlorine (2 wt % of Cl present in polyvinyl chloride) in the form of chlorinated compounds is sorbed by CaO to obtain $CaCl_2$.

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In all these processes, the use of the products as petrochemical feedstock is possible only after complete removal of chlorine-containing compounds. Elucidation of the mechanism of pyrolysis, cracking, gasification, and mechanochemical processing and the development of possible alternative approaches to chlorinated waste recycling became the subject of research in the past 15 years. These processes will be considered in detail in the next sections.

PYROLYSIS

Processes for pyrolysis of polyvinyl chloride containing waste can be subdivided into several types:

– noncatalytic and catalytic pyrolysis; in catalytic pyrolysis, the addition of a catalyst accelerates the dechlorination, and the addition of a sorbent decreases the chlorine content of the products;

– pyrolysis of pure polyvinyl chloride and of mixtures containing polyvinyl chloride (binary and multicomponent mixtures with polyvinyl chloride, chlorine- and bromine-containing mixtures, municipal plastics waste, joint pyrolysis of polyvinyl chloride waste and biomass);

– one- and two-step pyrolysis. In the first case, dechlorination of polyvinyl chloride waste and cracking of degradation products occur simultaneously; in the second case, chlorine-containing compounds are removed either in the head of the process (polyvinyl chloride degradation with the addition of a sorbent) or at its end (addition of a sorbent to pyrolysis products).

Pyrolysis of pure polyvinyl chloride without impurities. Polyvinyl chloride pyrolysis is a two-step process (Fig. 5) [30]. The first step involves dehydrochlorination of the polymer with the formation of conjugated double bonds, which are cleaved in the second step. The main labile sites in dehydrochlorination are tertiary chlorine atoms. In the second step, degradation of the dehydrochlorinated product continues and involves cracking and pyrolysis of linear or cyclic hydrocarbons with low carbon content. The conjugated polyene structure formed upon release of HCl and containing both cis and trans fragments undergoes aromatization/cyclization and cross-linking with the formation of a wide range of hydrocarbon products.

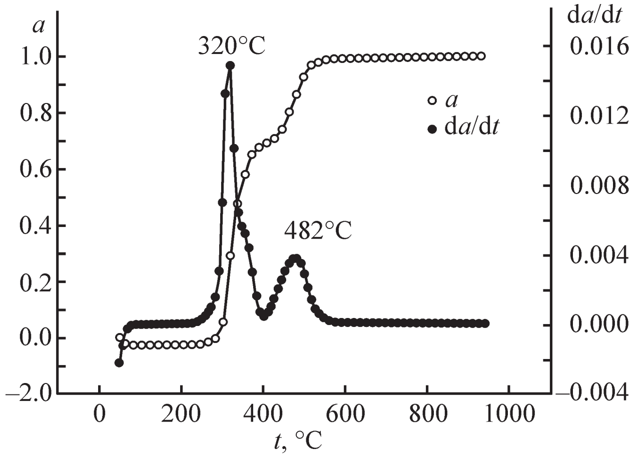

Fig. 5. Thermogravimetric curve of polyvinyl chloride degradation [30].[5]

The first step of the polyvinyl chloride pyrolysis occurs in the interval 280–400°C and is accompanied by 65% weight loss (in terms of the total residue); the weight loss maximum in the first step is observed at 320°C. The second step of the polyvinyl chloride pyrolysis occurs in the interval 400–560°C with up to 35% weight loss; the weight loss maximum in the second step is observed at 482°C. The first degradation step is faster than the second step. The pyrolysis products consist of hydrogen chloride (56%), benzene and its derivatives (6.3%), hydrocarbon gases (28.6%), and solid semicoke (9.1%) [31]; the degree of dechlorination is 99% (Table 1).

The use of a reactor with a wire grid in polyvinyl chloride pyrolysis reduced to a minimum the reactions between the released volatiles and the polyvinyl chloride particles undergoing pyrolysis and the secondary reactions of volatile components [32]. At the pyrolysis temperature increased to 500°C, the semicoke yield decreased to 16% (Fig. 6), and the fraction of chlorine atoms in polyvinyl chloride decreased from 55 to 1%.

A study of the pyrolysis mechanism has shown that, at temperatures lower than 450°C, the weight loss is mainly due to dehydrochlorination, whereas at elevated temperatures (<450°C) the major weight loss is due to the release of hydrocarbons. At 450°C, 88% of the weight loss is due to dehydrochlorination and only 12%, to the release of hydrocarbons. This means that the cyclization/aromatization process starts in the early step, whereas the formation and release of aromatic hydrocarbons occur in the late step of the dehydrochlorination.

Along with the formation of chlorinated organic compounds, the formation of polycyclic aromatic

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Table 1. Characteristics of catalytic pyrolysis of polyvinyl chloride

Polymer	Chlorine content, %	Additive	Substrate/additive	Conditions	Results	References
Polyvinyl chloride	56.5	–	–	520°C, N_2	56% HCl, 6.3% benzene and its derivatives, 28.6% gaseous hydrocarbons, 9.1% solid residue	[31]
Polyvinyl chloride	55	–	–	500°C, N_2	54% HCl, 16% solid residue	[32]
Polyvinyl chloride	56.32	–	–	500–900°C, N_2	54.7% HCl, 21% tar, 20% coke, 4.3% gaseous hydrocarbons (500°C) 30.2% HCl, 14% tar, 36% coke, 19.8% gaseous hydrocarbons (900°C)	[33]
Polyvinyl chloride	54.8–55.6	–	–	1 h, 150°C + 1 h, 430°C, N_2	54.1% HCl	[35]
Polyvinyl chloride waste	53.3	–	–	1 h, 150°C + 1 h, 430°C, N_2	51.5% HCl	[35]
Polyvinyl chloride/ petroleum residues (4/6)		–	–	1 h, 150°C + 1 h, 430°C, N_2	20.6% HCl	[35]
Polyvinyl chloride	54.8–55.6	Fe_2O_3/C		350°C, 2 h, N_2	50.6% HCl	[35]
Polyvinyl chloride	–		Polyvinyl chloride/MeO = 2 : 1, where 1 mol of polyvinyl chloride corresponds to the structural unit C_2H_3Cl	30 min, 400°C, He 10 min, 800°C, He	800°C, 10 min, He, chlorobenzene/1 g of polyvinyl chloride	[36]
		–			0.15 mg	
		ZnO			0.03 mg	
		CaO			0.07 mg	
		Fe_2O_3			0.24 mg	
		PbO			0.07 mg	
		La_2O_3			0.06 mg	
		Nd_2O_3			0.15 mg	
		CeO_2			0.25 mg	
		Al_2O_3			0.09 mg	
Polyvinyl chloride	50.6	–	–	375°C, 850°C	10 and 20 ppm chlorobenzenes, 0.88 and 69 ppm chlorophenols	[38]
Polyvinyl chloride	50.6	–	–	850°C	10 ppm chlorobenzenes, 2.7 ppm chlorophenols	[38]
Polyvinyl chloride	50.6	Fe	Polyvinyl chloride /Fe (60/40)	375°C, 850°C	1300 and 33 ppm chlorobenzenes, 2400 and 602 ppm chlorophenols	[38]
Polyvinyl chloride waste		Electric arc furnace dust	Feedstock/additive (1 : 1, 1 : 2, 1 : 3)	0–1000°C, N_2	–	[39, 40]

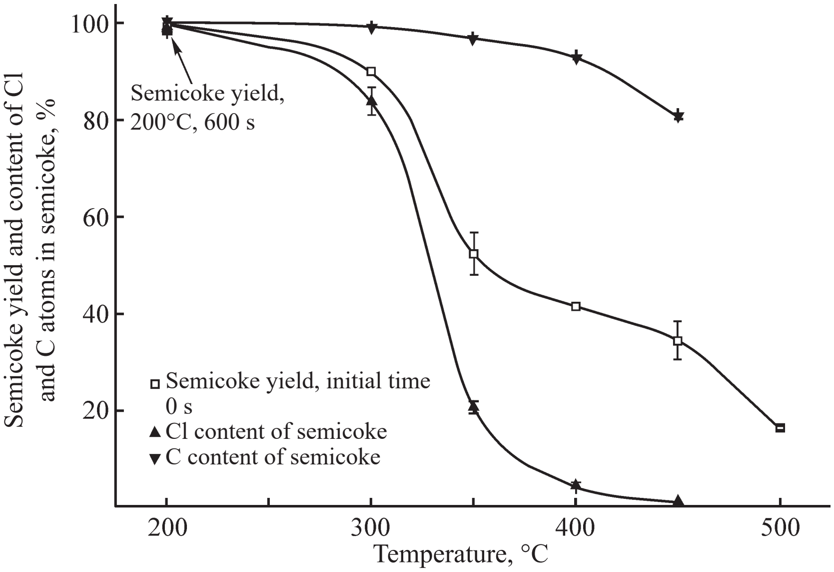


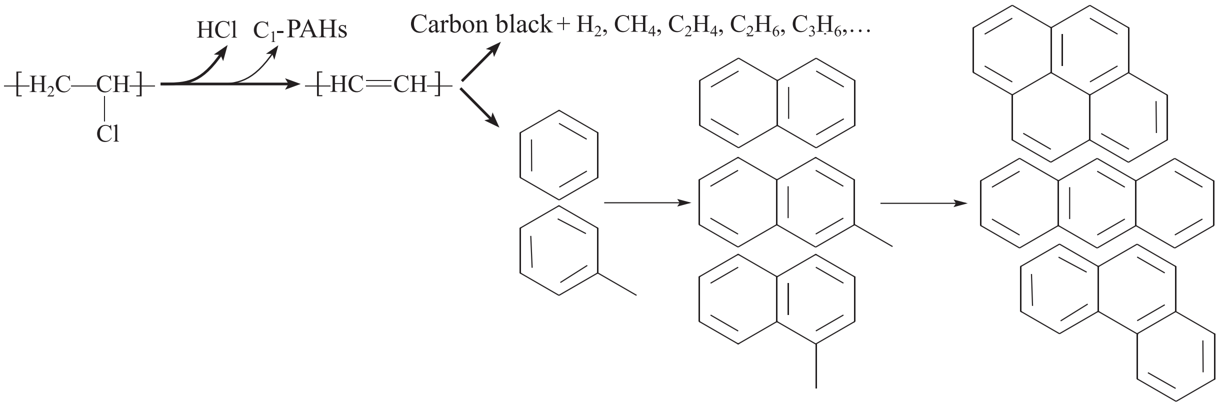
Fig. 6. Semicoke yield and content of chlorine and carbon atoms in the semicoke as functions of the pyrolysis temperature [32].[6]

hydrocarbons (Scheme 1) is one of the main drawbacks of polyvinyl chloride and, as a consequence, of pyrolysis of municipal plastics waste, because emission of these hydrocarbons negatively affects the human health [33]. A study of the effect of temperature on the formation of polycyclic aromatic hydrocarbons with 2–4 rings in polyvinyl chloride pyrolysis tar showed that the fraction of certain polycyclic aromatic hydrocarbons increased by a factor of 6–8 with an increase in the temperature to 900°C and that the yield of polycyclic aromatic hydrocarbons in slow pyrolysis was considerably lower than that in fast pyrolysis.

With an increase in the temperature from 500 to 900°C, the HCl yield decreased from 54.7 to 30.2%, whereas the volume of gaseous hydrocarbons increased. Slow pyrolysis favored higher yield of HCl and lower yield of the gas and tar, compared to fast pyrolysis in which incomplete dehydrochlorination of polyvinyl chloride led to the formation of chlorinated aromatic compounds.

The use of additives in polyvinyl chloride pyrolysis in many studies implies either acceleration of polyvinyl chloride dehydrochlorination due a decrease in the weight loss onset temperature [34] or a decrease in the

Scheme 1. Mechanism of formation of polycyclic aromatic hydrocarbons in the course of polyvinyl chloride pyrolysis.



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fraction of chlorine-containing compounds in reaction products due to binding of the released HCl with sorbents [3].

Two-step pyrolysis of pure polyvinyl chloride and wastes containing polyvinyl chloride was performed in [35]. In noncatalytic pyrolysis of pure polyvinyl chloride, the fraction of liquid oil was 16.9%; in pyrolysis of polyvinyl chloride waste, 12.1%; and in pyrolysis of polyvinyl chloride/petroleum residue mixture, 43.8%. The yield of gaseous HCl decreased in this series (Table 1). Addition of petroleum residues to polyvinyl chloride in 4/6 ratio led to a significant increase in the fraction of liquid oil and to a decrease in the fraction of HCl (20.6%) due to the reaction of asphaltenes with chlorine radicals formed in the course of polyvinyl chloride cracking. Chlorination of asphaltenes occurred very rapidly, as indicated by the release of a smaller amount of HCl. The results of catalytic pyrolysis of polyvinyl chloride over 5% Fe_2O_3/C differed from those of the noncatalytic process insignificantly: The fraction of gaseous HCl was 50.6, and that of the liquid oil, 11.1%, which shows that the catalyst is inefficient in polyvinyl chloride pyrolysis. When using the iron-containing catalyst, the fraction of soluble organic compounds increased to 36.6%, compared to 28.1% for pure polyvinyl chloride.

The effect of some metals (Al, Fe, Zn), metal oxides (Al, Ti, Cu, Fe, Ca oxides), and carboxylates (Zn, Sn carboxylates) on polyvinyl chloride pyrolysis at 350–550°C was studied by Blazso and Jakab [34]. The metals and oxides interacted with polyvinyl chloride via surface contacts without stirring. Fe and Zn metals, Fe and Cu oxides, and zinc carboxylates, in which the cation radius is relatively large, favored a decrease in the dechlorination temperature due to the formation of metal chlorides.

Aluminum does not influence the amount of the HCl released in the course of the polyvinyl chloride degradation because of the presence of a passivating surface oxide layer, preventing the reaction with HCl. The formation of benzene from polyvinyl chloride involves not only the removal of three HCl molecules from a segment of six carbon atoms, but also the separation of the preliminarily formed cyclohexadiene fragment from the polymer chain. A decrease in the yield of benzene and toluene is also associated with the inhibiting effect of iron and zinc. Aluminum favors the formation of HCl and increases the fraction of alkylaromatic compounds. The dechlorination of polyvinyl chloride in the presence of aluminum yields naphthalene and anthracene along with benzene. The presence of aluminum oxide and titanium dioxide leads to an increase in the polyvinyl chloride dechlorination temperature and in the process rate.

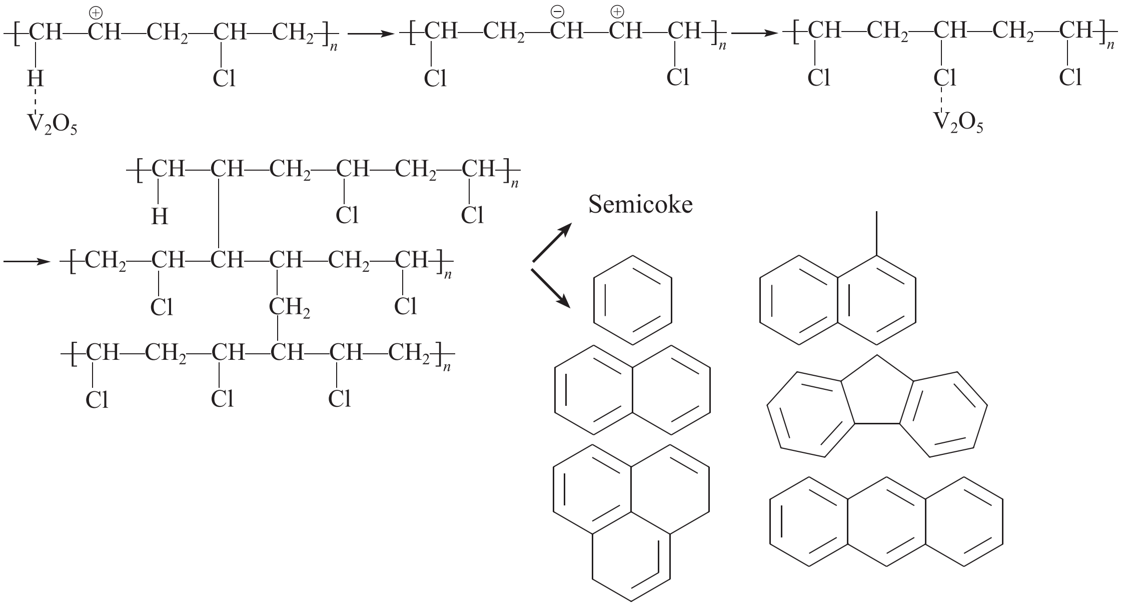
Pyrolysis of polyvinyl chloride in the presence of metal oxides, including rare earth metal oxides, was performed by Masuda et al. [36]. The major components of liquid products were aromatic hydrocarbons C_6–C_{14}, including benzene and toluene. On adding Fe_2O_3 and ZnO, the amount of liquid products decreased considerably: by 30% relative to the amount of oils formed by pyrolysis of pure polyvinyl chloride. On adding Al_2O_3, it, on the contrary, increased; the fraction of benzene and toluene increased also. High yield of gaseous CO and CO_2 in the polyvinyl chloride/Fe_2O_3 mixture is due to the reduction of iron oxide to the metal under these conditions. In the presence of Al_2O_3, the fraction of gaseous products was 70% lower than in pyrolysis of pure polyvinyl chloride. The presence of PbO and rare earth metal oxides did not influence the yield of gases compared to pure polyvinyl chloride. The semicoke formation increased on adding ZnO, whereas CaO favored a decrease in the carbon fraction in the residue.

In the course of pyrolysis, chlorine is released from polyvinyl chloride not only in the form of gaseous HCl, which chlorinates metal oxides to oxychlorides and chlorides, but also in the form of chlorinated organic compounds, as shown previously [3]. Fe_2O_3 and CeO_2 as Lewis acids favor Friedel–Crafts halogenation of benzene with the formation of chlorobenzene (Table 1), whereas ZnO suppresses this process.

Rare earth metal oxides (La_2O_3, Nd_2O_3, CeO_2) demonstrated excellent ability to take up a large amount of chlorine initially present in polyvinyl chloride [36]. For example, the addition of La_2O_3 favored the chlorine removal from polyvinyl chloride in the form of LaOCl with more than 95% efficiency at 800°C and 75% efficiency at 400°C. At 800°C, PbO bound up to 70% of the released HCl with the formation of lead chloride, whereas Fe_2O_3 and CeO_2 took up only 20–30% of HCl. Al_2O_3 was not chlorinated under these conditions because of its inertness.

As in the previous studies, the addition of oxides of transition metals such as V, Mo, Ti, Cu, Zn, and Mn favored a decrease in the initial temperature of the two

Scheme 2. Action mechanism for transition metal oxides of the first type.



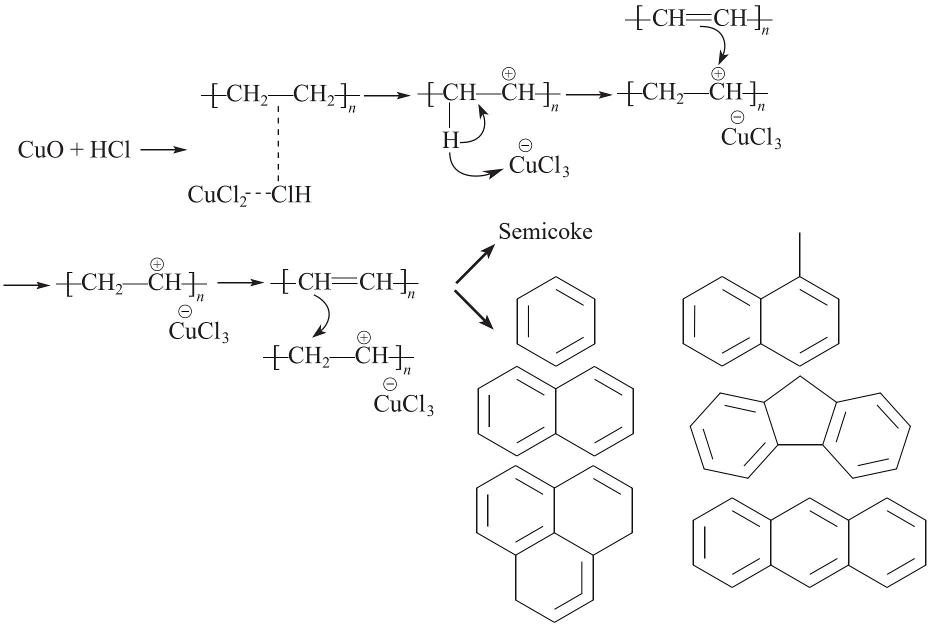
steps of the polyvinyl chloride pyrolysis [37]. The use of these oxides as highly efficient fume suppressants led to a decrease in the amount of the aromatic compounds formed and to a significant increase in the content of aliphatic compounds in volatiles (700°C, N_2). Thus, these oxides prevented the formation of polyolefin structures, thus reducing the toxicity of volatile pyrolysis products. Transition metal (V, Mo, Ti) oxides favored the intermolecular cross-linking, forming a stable structure of a physical bridging bond and reducing the formation of polycyclic aromatic hydrocarbons. The catalytic properties of the oxides decreased in the order $V_2O_5 > MoO_3 > TiO_2$. The metal cation in the oxide formed a hydrogen bond with hydrogen ions in polyvinyl chloride (Scheme 2). Mo^{6+} in MoO_3 inhibited the cyclization of polyvinyl chloride chains to aromatic and toxic compounds.

Cu, Zn, and Mn oxides favored the formation of the cross-linked structure owing to the reaction with the released HCl, thus preventing the formation of polycyclic aromatic hydrocarbons. The metal chlorides formed in the process interacted with the chlorine atom of the polymer to form an electrophilic complex (Scheme 3), which favored the formation of cross-links between the molecules via electrophilic addition. The efficiency of the binding of chlorine atom with metal oxides decreased in the order CuO > ZnO > MnO_2. The use of MnO_2 led to a decrease in the HCl formation rate, whereas CuO favored the polyvinyl chloride dehydrochlorination in the first step of the pyrolysis. The addition of zinc led to the formation of a carbon layer, decreasing the formation of polyenes and volatile aromatic compounds, and to a decrease in the fume concentration and toxicity.

The use of oxides of all the above metals (V, Mo, Ti, Cu, Zn, and Mn) favored an increase in the amount of residual carbon in the system and formation of carbonized layer.

Font et al. performed one- and two-step combustion of pure polyvinyl chloride and polyvinyl chloride/iron nanoparticles (60/40) mixture at 850°C and in two steps (375 and 850°C) [38]. The polyvinyl chloride combustion occurred in two steps: thermal degradation with the release of HCl and benzene and subsequent combustion of the carbon residue. The presence of iron nanoparticles accelerated the dehydrochlorination owing to a decrease in the weight loss onset temperature, as in [34]. For example, chlorobenzene and chlorophenols were detected in combustion products in all the cases; the presence of Fe nanoparticles increased their amount by a factor of 10–30. Iron chloride, which is formed in the course of combustion of the polyvinyl chloride/Fe mixture and acts as a Lewis acid, favors the intermolecular cyclization of the polyene chain (intramolecular cyclization does not occur), which led to the formation of unsubstituted aromatic compounds

Scheme 3. Action mechanism for transition metal oxides of the second type.



such as benzene and certain polycyclic aromatic hydrocarbons and to their chlorination.

The intermediate polymer chain formed by the polyvinyl chloride dehydrochlorination in an He/O_2 mixture undergoes catalytic oxychlorination under the action of $FeCl_3$, which leads to the formation of toxic polychlorinated dibenzodioxins in an amount as large as 8217 thousand pg per gram of polyvinyl chloride, whereas without Fe only 183 pg of these toxicants was formed per gram of polyvinyl chloride.

Al-Harahsheh et al. [39, 40] studied the kinetics of pyrolysis of polyvinyl chloride waste mixed with electric arc furnace dust (EAFD), which is a by-product of metallurgical processes and is formed in electric arc furnaces in the course of steel smelting. The dust toxicity is caused by the presence of heavy metal compounds: zincite (ZnO), franklinite ($ZnFe_2O_4$), magnetite (Fe_3O_4), hematite (Fe_2O_3), halite (NaCl), sylvite (KCl), lead hydroxychloride (PbOHCl), etc.

Owing to fast reaction of the released HCl with metal oxides, the weight loss onset temperature decreased. The total weight loss in the first step of the pyrolysis of polyvinyl chloride/EAFD mixtures with 1 : 1, 1 : 2, and 1 : 3 ratios was 21.5, 32, and 39%, respectively, which is lower than for pure polyvinyl chloride (45–55%), and an increase in the residual weight associated with the formation of metal chlorides in the solid phase was 26, 20, and 16.5%, respectively. The yield of benzene as a result of the cyclization and decomposition of the polyene formed by the hydrogen chloride release from polyvinyl chloride increased also. Mass-spectrometric analysis revealed the formation of methanol and propyne at temperatures higher than 350°C. Metal oxides remained in the pyrolysis residue, whereas Zn and Pb transformed into soluble metal chlorides, which could be subsequently recovered by leaching in water.

In all the cases, the use of catalysts accelerated the polyvinyl chloride dechlorination. Some of the catalysts such as Fe_2O_3 and CeO_2 [3], owing to their acid properties, favored the formation of chlorinated organic compounds in pyrolysis oil and decreased the fraction of pyrolysis oil in the products [34]. Basic oxides (La_2O_3 [3], CaO [32, 34]) and amphoteric ZnO acted as sorbents binding the released hydrogen chloride and thus decreased the content of chlorine-containing compounds both in gaseous products and in liquid oils. The metal chlorides in the solid residue were removed, as a rule, by leaching. Combustion of polyvinyl chloride particles at high temperatures [38] in the presence of iron particles led to significant formation not only of chlorobenzenes and chlorophenols, but also of more hazardous polychlorinated dibenzodioxins. The results obtained in laboratory experiments on using metals and their oxides in pyrolysis of pure polyvinyl chloride can be applied to pyrolysis of mixtures containing polyvinyl chloride.

Pyrolysis of binary mixtures containing polyvinyl chloride. Polyvinyl chloride [30] starts to degrade at 250–260°C. The degradation occurs in two steps. In the interval 250–360°C, HCl is completely removed, and 54.2 wt % carbon-containing residue is formed; at $T \geq 410$°C, the remaining polyene structure undergoes degradation and cyclization with the formation of 15 wt % residue (Fig. 7) [41]. Poly(ethylene terephthalate) degrades at 400–500°C to leave approximately 15 wt % solid residue, which, in turn, degrades at higher temperature (>640°C). The polystyrene degradation starts at 300 and is complete at 490°C with the formation of 1.5 wt % residue. Polypropylene and polyethylene degrade at higher temperatures: 420–530 and 450–550°C, respectively. Acrylonitrile–butadiene–ethylene–styrene copolymer, as a rule, degrades in one step at 349–514°C to leave only 1.7 wt % solid residue [42].

According to Wu et al. [43], the degradation rate maxima for pure polyvinyl chloride were observed at 321 and 493°C. The addition of polyethylene, polystyrene, and polyethylene/polystyrene mixture did not alter the dechlorination onset temperature, and only the temperature of the second step (cyclization/aromatization, cross-linking, and cracking) changed. For example, the second step of the degradation of the 1 : 1 polyethylene/polyvinyl chloride mixture occurred at a maximal rate at 507°C; i.e., the addition of polyethylene favored an increase in the polyvinyl chloride degradation temperature. The addition of polystyrene and of polyethylene/polystyrene mixture, on the contrary, decreased this temperature to 462 and 456°C.

Uddin et al. [44] studied the effect of polypropylene, low-density polyethylene, and polystyrene on the two-component pyrolysis of mixtures containing polyvinyl chloride. The pyrolysis temperature was 380°C for the polypropylene/polyvinyl chloride mixture, 430°C for the polyethylene/polyvinyl chloride mixture, and 360°C for the polystyrene/polyvinyl chloride mixture. The choice of the temperature was governed by the degradation temperatures of the components mixed polyvinyl chloride. In all the cases, the addition of a second polymer to polyvinyl chloride led to an increase in the fraction of liquid oils relative to pure polyvinyl chloride. The yield of pyrolysis oils decreased in the order polypropylene/polyvinyl chloride (73%) > polyethylene/polyvinyl chloride (69%) > polystyrene/polyvinyl chloride (60%); the higher yield of the solid residue (27%) consisting of semicoke and heavy hydrocarbons was reached in the case of degradation of the polystyrene/polyvinyl chloride mixture. The major fraction of chlorine from polyvinyl chloride was released in the form of gaseous HCl (91–96%). Owing to the reaction of the hydrogen chloride released from polyvinyl chloride with the monomers formed from polystyrene, polypropylene, and polyethylene, the fraction of chlorinated organic compounds considerably increased (to 3–12%) relative to their fraction in pyrolysis of pure polyvinyl chloride [39]. The content of chlorinated organic compounds in liquid products decreased in the order polypropylene/polyvinyl chloride > polystyrene/polyvinyl chloride > polyethylene/polyvinyl chloride (from 12 700 to 2800 ppm, Table 2). The major components in pyrolysis oils were monomers of polypropylene, polystyrene, and polyethylene, respectively, and their derivatives.

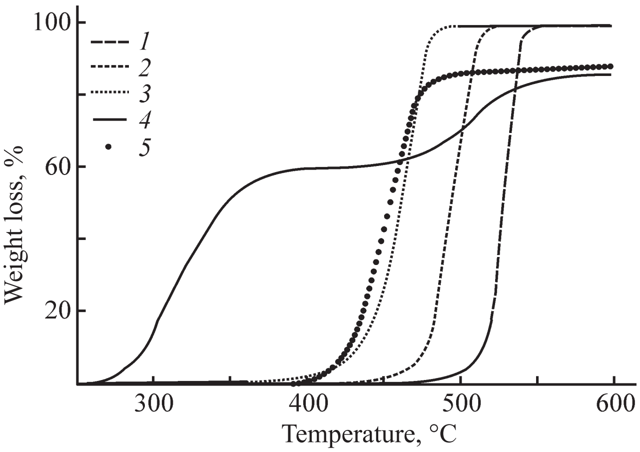


Fig. 7. Thermogravimetric curves of (*1*) polyethylene, (*2*) polypropylene, (*3*) polystyrene, (*4*) polyvinyl chloride, and (*5*) poly(ethylene terephthalate) [41].

Pyrolysis of the polystyrene/polyvinyl chloride mixture [45] at the pyrolysis temperature of the polyethylene/polyvinyl chloride mixture (430°C) in an N_2 stream led to an increase in the yield of oils (67.7%), and pyrolysis of the polypropylene/polyvinyl chloride mixture [45], on the contrary, to a decrease in their yield (56.7%) as compared to the pyrolysis of the mixtures in [44]. The increase in the pyrolysis temperature led to the formation of a smaller amount of chlorinated organic compounds in pyrolysis oils: 81 ppm in the case of the polystyrene/polyvinyl chloride mixture and 365 ppm

Table 2. Conditions of catalytic pyrolysis of binary mixtures

Polymer/copolymer	Chlorine content, %	Additive	Substrate/additive	Conditions	Degree of dechlorination	References
PP/PVC (4 : 1), 10 g	52.8 in PVC	–	–	380°C, N_2	~100% (8.8% in oil, 89.4% HCl)	[44]
PS/PVC (4 : 1), 10 g	52.8 in PVC	–	–	360°C, N_2	~100% (4.2% in oil, 91.8% HCl)	[44]
PE/PVC (4 : 1), 10 g	52.8 in PVC	–	–	430°C, N_2	~100% (1.8% in oil, 96.6% HCl)	[44]
PP/PVC (4 : 1), 10 g	52.8 in PVC	–	–	430°C, N_2	~100% (0.2% in oil, 98% HCl)	[45]
PS/PVC (4 : 1), 10 g	52.8 in PVC	–	–	430°C, N_2	~100% (0.5% in oil, 92.3% HCl)	[45]
PVDC, 10 g	73.2	–	–	430°C, N_2	~100% (68% HCl, 32% in solid residue)	[46]
PP/PVDC (9 : 1), 10 g	73.2 PVDC	–	–	430°C, N_2	~100% (98.2% HCl, 0.2% chlorinated organic compounds)	[46]
PE/PVDC (9 : 1), 10 g	73.2 PVDC	–	–	430°C, N_2	~100% (91.3% HCl, 0.1% chlorinated organic compounds)	[46]
PS/PVDC (9 : 1), 10 g	73.2 PVDC	–	–	430°C, N_2	~100% (83.9% HCl, 2% chlorinated organic compounds)	[46]
PP/PVC (4 : 1), 10 g	51.5 in PVC	–	–	400°C, N_2	80% HCl 20% chlorinated organic compounds)	[47]
PP/PVC (4 : 1), 10 g	51.5 in PVC	MgO	PP/PVC/MgO = 4/1/1	400°C, N_2	95.7% (8.7% HCl, 5% chlorinated organic compounds)	[47]
PP/PVC (4 : 1), 10 g	51.5 in PVC	MgO/C	PP/PVC/MgO/C = 4/1/1	400°C, N_2	97.1% (1.1% HCl, 1% chlorinated organic compounds)	[47]
PP/PVC (4 : 1), 10 g	51.5 in PVC	La–MgO	PP/PVC/La–MgO = 4/1/1	400°C, N_2	99% (0.54% HCl, 0.11% chlorinated organic compounds)	[48]
PP/PVC (4 : 1), 10 g	51.5 in PVC	Al–Mg oxide	PP/PVC/Al–Mg = 4/1/1	380°C, N_2	~100% (6.1% HCl, 2.8% chlorinated organic compounds)	[49]
PP/PVC (4 : 1), 10 g	51.5 in PVC	MgO	PP/PVC/MgO = 4/1/1	380°C, N_2	~100% (29% HCl, 3.7% chlorinated organic compounds)	[49]
PP/PVC (4 : 1), 10 g	51.5 in PVC	γ-Al_2O_3	PP/PVC/γ-Al_2O_3 = 4/1/1	380°C, N_2	~100% (82.3% HCl, 8.1% chlorinated organic compounds)	[49]

Table 2. (Contd.)

Polymer/copolymer	Chlorine content, %	Additive	Substrate/additive	Conditions	Degree of dechlorination	References
PE/PVC (4 : 1), 10 g	51.5 in PVC	Al–Mg oxide	LDPE/PVC/Al–Mg = 4/1/1	420°C, N_2	~100% (5.7% HCl, 1.1% chlorinated organic compounds)	[49]
PS/PVC (4 : 1), 10 g	51.5 in PVC	Al–Mg oxide	PE/PVC/Al-Mg = 4/1/1	360°C, N_2	100% (6.5% HCl, 1.5% chlorinated organic compounds)	[49]
PP/PVC (4 : 1), 10 g	52.8 in PVC	Al_2O_3–SiO_2, FeOOH, Fe_2O_3, Fe_3O_4	Mixture/catalyst= 10/1 Mixture/sorbent = 5/1	380°C, N_2	~100% (0.8% chlorinated organic compounds)	[44]
PE/PVC (4 : 1), 10 g	52.8 in PVC	–	–	430°C, stream N_2	97.3% (96.2% HCl, 0.1% chlorinated organic compounds)	[45]
PE/PVC (4 : 1), 10 g	52.8 in PVC	Al_2O_3–SiO_2	Mixture/catalyst= 10/1	430°C, stream N_2	~100% (82.7% HCl, 0.7% chlorinated organic compounds)	[45]
PE/PVC (4 : 1), 10 g	52.8 in PVC	γ-Fe_2O_3	Mixture/sorbent = 5/1	430°C, stream N_2	~100% (34.7% HCl, 0.2% chlorinated organic compounds)	[45]
PE/PVC (4 : 1), 10 g	52.8 in PVC	RedMud	Mixture/sorbent = 5/1	430°C, stream N_2	~100% (23.1% HCl, 0.26% chlorinated organic compounds)	[45]
PP/PVC (4 : 1), 10 g	52.8 in PVC	RedMud	Mixture/sorbent = 5/1	430°C, stream N_2	~100% (29.9% HCl, 0.39% chlorinated organic compounds)	[45]
PS/PVC (4 : 1), 10 g	52.8 in PVC	RedMud	Mixture/sorbent = 5/1	430°C, stream N_2	~100% (22.1% HCl, 0.25% chlorinated organic compounds)	[45]
LDPE waste/PVC waste (96%/4%) 200 g	0.2 in LDPE, 21.5 in PVC	–	–	400, 700°C, stream N_2	~100%, 500 ppm in oil	[51]
LDPE waste/PVC waste (96%/4%) 200 g	0.2 in LDPE, 21.5 in PVC	CaO	Mixture/sorbent = 200 g/ 400 g	400, 700°C, stream N_2	~100%, 9.25 ppm in oil	[51]

Note: PP, polypropylene; PVC, polyvinyl chloride; PS, polystyrene; PE, polyethylene; PVDC, polyvinylidene chloride; and LDPE, low-density polyethylene.

in the case of the polypropylene/polyvinyl chloride mixture [45].

The effect of the addition of acrylonitrile–butadiene–ethylene–styrene copolymer on the pyrolysis of polyvinyl chloride was studied at various weight ratios of the mixture components (1/3, 1/1, 3/1) [42]. The major components of the pyrolysis oil obtained from the acrylonitrile–butadiene–ethylene–styrene copolymer were its monomers, i.e., styrene, benzene, α-methylstyrene, and phenylvaleronitrile. The interaction of acrylonitrile–butadiene–ethylene–styrene copolymer and polyvinyl chloride in the mixture led to earlier decomposition both of polyvinyl chloride with the acceleration of the HCl evolution and of acrylonitrile–butadiene–ethylene–styrene copolymer. In the first step, polyvinyl chloride underwent dechlorination with the weight loss of acrylonitrile–butadiene–ethylene–styrene copolymer/polyvinyl chloride mixtures of 15, 29.4, and 41.9% at the 75/25, 50/50, and 25/75 ratios, respectively (243–378°C), whereas in the second step the weight loss, owing to the copolymer degradation, the weight loss was 76.3, 56.3, and 40.5%, respectively (367–533°C). The first weight loss peaks for the 75/25, 50/50, and 25/75 mixtures were recorded at 304, 311, and 317°C, whereas for pure polyvinyl chloride this temperature was 322°C. The fraction of the solid residue increased to 17.6% with an increase in the polyvinyl chloride content.

Bhaskar et al. [46] compared the pyrolysis of polyvinylidene chloride and polyvinyl chloride, both pure and in mixtures with polypropylene, polyethylene, and polystyrene. The pyrolysis of pure polyvinylidene chloride was accompanied by the formation of 68% gases and 32% solid residue, in contrast to pure polyvinyl chloride [35], without liquid products owing to higher chlorine content (73.2 wt % Cl) and lower degradation temperature. Polyvinylidene chloride starts to degrade already at 200°C against 250°C for polyvinyl chloride, and 50% weight loss occurs at 300°C against 350°C for polyvinyl chloride. The pyrolysis of binary mixtures, i.e., the addition of other polymers to polyvinylidene chloride, leads to the formation of 61–74% pyrolysis oil owing to a decrease in the fraction of gases and solid residue; in contrast to pure polyvinylidene chloride, the amount of the solid residue did not exceed 5–9%.

The formation of chlorinated hydrocarbons in liquid products decreased in the order polystyrene/polyvinylidene chloride > polypropylene/polyvinylidene chloride > polyethylene/polyvinylidene chloride, with the content of chlorine-containing compounds in the products being several times lower than in the corresponding mixtures with polyvinyl chloride, despite higher content of chlorine atoms in polyvinylidene chloride compared to polyvinyl chloride. This fact can be attributed to the release of the major fraction of chlorine from polyvinylidene chloride at lower temperatures than from polyvinyl chloride and to the degradation of polyethylene, polypropylene, and polystyrene. The highest content of chlorinated hydrocarbons in oils obtained from the polystyrene/polyvinylidene chloride mixture was due to higher reactivity of the styrene monomer, compared to other unsaturated hydrocarbons, toward HCl.

The major chlorine-containing products in the pyrolysis oil were 2-chloro-2-methylpropane and 2-chloro-2-methylpentane in the case of polyethylene/polyvinylidene chloride and polypropylene/polyvinylidene chloride mixtures and 2-chloroethylbenzene and 2-chloro-2-phenylpropane in the case of polystyrene/polyvinylidene chloride mixture, as in the analogous mixtures with polyvinyl chloride.

The use of sorbents is necessary for binding the released hydrogen chloride. This leads, as a rule, to a decrease in the content of gaseous chlorine and chlorine in liquid products. The major fraction of chlorine released in the course of polyvinyl chloride degradation remains in the solid residue in the form of metal chlorides.

Zhou et al. [47] used MgO and MgO/C as HCl sorbents in pyrolysis of the polypropylene/polyvinyl chloride mixture. The MgO/C composite was prepared by the reaction of $Mg(OH)_2$ with sucrose used as a carbon source. Carbon, in turn, prevented the agglomeration of the synthesized MgO nanoparticles. The interaction of the MgO/C sorbent with the HCl released in the course of pyrolysis was enhanced as compared to MgO owing to larger surface area and smaller particle size of MgO/C, and the presence of carbon in the composite favored the decomposition of chlorinated organic compounds formed in the process (Table 2).

In noncatalytic pyrolysis of the polypropylene/polyvinyl chloride mixture, the fraction of HCl was 80%, and that of chlorinated organic compounds, 20%. With the addition of sorbents, the fraction of the released hydrogen chloride and chlorinated organic compounds decreased considerably: to 13.7% over MgO and to 2.1% over MgO/C. In the latter case, HCl makes up 1.1%, and chlorinated hydrocarbons such as 2-chloro-

2-methylpropane, 2-chloro-2-methylbutane, 2-chloro-2-methylpentane, and 3-chloro-3-methylpentane make up 1%. The remaining chlorine (about 95% over MgO/C and about 82% over MgO) passed into magnesium chloride.

The addition of La to MgO appreciably accelerated the degradation of the polypropylene/polyvinyl chloride mixture and led to a decrease in the mean number of carbon atoms in the liquid products [48] (to 10 over La–MgO against 20 over MgO), which can be attributed to a considerable increase in the number of acid sites in the catalyst due to the addition of La_2O_3, and also to larger surface area of the La-containing catalyst. As compared to the results obtained in pyrolysis of the polymer mixture in the presence of MgO and MgO/C [47], enhanced interaction of the La–MgO sorbent [36] with hydrogen chloride released in the course of the polyvinyl chloride degradation led to a decrease in the HCl fraction to 0.54% and in the fraction of chlorinated organic compounds to 0.11%. Because of the formation of an $MgCl_2$ "crust" on the surface of the MgO catalyst, reducing the catalyst performance in further dehydrochlorination of polyvinyl chloride, this catalyst could not be reused, whereas La–MgO was active and stable in the course of five cycles.

Zhou et al. [49] studied the effect of sorbents and catalysts on the chlorine removal in pyrolysis of polypropylene/polyvinyl chloride, low-density polyethylene/polyvinyl chloride, and polystyrene/polyvinyl chloride mixtures at temperatures determined by the degradation temperatures of the polymers mixed with polyvinyl chloride. In pyrolysis of the polypropylene/polyvinyl chloride mixture, the fraction of gaseous HCl decreased from 82.3 to 6.1% in the series γ-Al_2O_3 > MgO > Al–Mg, where Al–Mg is a composite oxide prepared by precipitation of metal salts in an alcoholic NH_3 solution with the subsequent calcination, whereas the fraction of hydrogen chloride released in the course of the noncatalytic pyrolysis of the mixture was 88.2%. Similarly, the fraction of chlorinated organic compounds decreased to 2.8%, whereas in the noncatalytic pyrolysis products their fraction was 11.7%. High performance of the composite catalyst compared to the other additives was associated with acid–base properties of its components, mutually enhancing each other: MgO exhibited high dechlorinating power owing to its base properties, and γ-Al_2O_3 exhibited cracking power owing to acid properties.

Similar enhanced performance of the composite Al–Mg catalyst was observed in pyrolysis of the low-density polyethylene/polyvinyl chloride and polystyrene/polyvinyl chloride mixtures: This catalyst bound 17–19 times larger amount of gaseous hydrogen chloride and decreased the fraction of organic chlorine by a factor of 3–4 compared to the noncatalytic pyrolysis. Up to 91–93% of the released HCl was converted to metal chlorides in the reaction with the composite.

Uddin et al. [44] considered simultaneous use of the Al_2O_3–SiO_2 catalyst (SA-1) and sorbents based on iron oxides (FeOOH, Fe_2O_3, Fe_3O_4) in pyrolysis of the polypropylene/polyvinyl chloride mixture. As in [49], the addition of Al_2O_3–SiO_2 favored considerable acceleration of the polymer degradation and a decrease in the relative amount of the liquid products, and the sorbents decreased the relative content of chlorinated organic compounds. The best result was reached in the vapor-phase contact with a mixture of the catalyst and sorbent: 1100 ppm chlorinated hydrocarbons (C_6–C_{10}) in the liquid phase, whereas the pyrolysis oil formed by degradation of the polypropylene/polyvinyl chloride mixture contained 12700 ppm organic chlorine. Among iron-containing sorbents, FeOOH and Fe_3O_4 showed the highest performance.

The catalytic and dechlorinating properties of the SA-1 catalysts and γ-Fe_2O_3 and RedMud (mixture of metal oxides) sorbents in pyrolysis of the polyethylene/polyvinyl chloride mixture were compared in [45]. The fraction of gaseous HCl released in the course of the polyvinyl chloride degradation decreased to 23.1% in the order no catalyst > SA-1 > γ-Fe_2O_3 > RedMud. As in [44], SA-1 showed only catalytic properties in polyvinyl chloride degradation. Higher absorbing ability of RedMud was caused by larger adsorption of HCl on the sorbent surface compared to γ-Fe_2O_3 [50]. Lower content of organic chlorine in the liquid oil of the noncatalytic pyrolysis (0.1%) compared to the catalytic pyrolysis (0.2–0.7%) was caused by the effect of the N_2 stream partially suppressing the reaction between gaseous HCl and polymer degradation products. As in the case of the polyethylene/polyvinyl chloride mixture, in pyrolysis of the polypropylene/polyvinyl chloride and polystyrene/polyvinyl chloride mixtures lower content of chlorinated compounds in the oil was observed in noncatalytic pyrolysis: 0.19 and 0.05%, respectively, whereas with RedMud less HCl was released and more solid residue was formed.

Park et al. [51] studied the two-step pyrolysis of the waste of low-density polyethylene and polyvinyl chloride (m = 200 g) in the presence of quick lime. The first step involved dechlorination of the mixture in a worm reactor (400°C), and the second step, complete degradation of low-density polyethylene and of the polyene formed from polyvinyl chloride in a fluidized-bed reactor (700°C). The major components of pyrolysis gases were methane, ethylene, ethane, propylene, butane, and 1,3-butadiene; the total yield of unsaturated monomers varied from 23 to 29% depending on the conditions. In the fluidized-bed reactor, pyrolysis oils enriched in aromatic compounds (up to 95%), including up to 51–80% monocyclic hydrocarbons, were obtained; the benzene yield considerably increased on adding lime.

When performing the pyrolysis without sorbent, the pyrolysis oil from the worm reactor contained about 2500 ppm chlorinated organic compounds; in the second step, their fraction decreased to 500 ppm. When feeding quick lime together with the polymer, the content of organic chlorine in the oil from the worm reactor (443 ppm) was lower than that in the oil from the fluidized-bed reactor (578 ppm), which is due to the reaction of calcium oxide with chlorine released in the worm reactor from polyvinyl chloride. The best result was obtained when using the hot lime filter in the second step: The content of chlorinated hydrocarbons in the pyrolysis oil obtained was as low as 9.25 ppm.

The addition of polypropylene, polystyrene, polyethylene, or acrylonitrile–butadiene–ethylene–styrene copolymer to polyvinyl chloride led to an increase not only in the fraction of liquid products but also in the content of chlorinated organic compounds in them owing to the reaction of the released hydrogen chloride in the course of the polyvinyl chloride degradation with the released monomers of polyethylene, polypropylene, polystyrene, and acrylonitrile–butadiene–ethylene–styrene copolymer. The addition of polyethylene in the polyethylene/polyvinyl chloride mixture decelerated the polyvinyl chloride degradation, whereas the addition of the polyethylene/polypropylene mixture and pure polypropylene considerably accelerated the second step of the degradation of dechlorinated polyvinyl chloride [43]. Pyrolysis of the mixtures in a stream of nitrogen [45], which partially suppresses the reaction between gaseous HCl and polymer degradation products, led to more efficient removal of chlorinated organic compounds compared to the process in an N_2 atmosphere [44]. Among the sorbents used, the best results were obtained with La–MgO [48], which also acts as a catalyst owing to its enhanced reaction with HCl (less than 0.11% chlorinated organic compounds in pyrolysis oils), and with RedMud [45] owing to its high absorption ability (0.2–0.4%). Also, less than 1% chlorinated organic compounds in liquid products were obtained at vapor-phase contact when using the catalyst and sorbent simultaneously [44]. The uptake of chlorine by CaO in the second step of the two-step pyrolysis in a semicommercial process allowed obtaining pyrolysis oil with the minimal content of chlorinated organic compounds, 9.25 ppm [51].

Pyrolysis of wastes containing polyvinyl chloride. Because wastes, as a rule, are mixtures containing various polymer components (including polypropylene, polyethylene, polystyrene, polyvinyl chloride, poly(ethylene terephthalate), etc.), it is necessary to study multicomponent systems similar in composition to municipal plastics wastes [6].

Many authors studied the pyrolysis of such model mixtures as polypropylene/polystyrene/polyethylene/polyvinyl chloride in 3 : 3 : 3 : 1 ratio (3P/PVC, where 3P denotes polypropylene/polystyrene/polyethylene) and polypropylene/polystyrene/polyethylene/polyvinyl chloride/poly(ethylene terephthalate) in 3 : 3 : 3 : 1 : 1 ratio (3P/PVC/PET) to evaluate the effect of several additives on the polyvinyl chloride dechlorination [6, 46, 49, 52, 53].

Noncatalytic pyrolysis of model mixtures 3P/PVC, 3P/PVC/PET, and MPW was studied by Bhaskar et al. [6]. The fraction of liquid products in pyrolysis of municipal plastics waste (59%) was higher than in pyrolysis of 3P/PVC/PET (53%) but lower than in pyrolysis of 3P/PVC (70%). Relatively high fraction of solid residue in the case of municipal plastics waste (16%) compared to model mixtures (5 and 13%) was due to the presence of various additives (plasticizers, stabilizers) in the polymer waste mixture.

The content of chlorinated compounds in liquid pyrolysis products increased in the order 3P/PVC < 3P/PVC/PET < MPW, which was associated with the presence of poly(ethylene terephthalate) in the model mixture and in municipal plastics waste. Poly(ethylene terephthalate) favored an increase in the fraction of chlorinated hydrocarbons in the oils and, as a consequence, to a sharp decrease in the fraction of

Table 3. Conditions of pyrolysis of wastes containing polyvinyl chloride

Polymer/copolymer	Chlorine content, %	Additive	Substrate/ additive	Conditions	Results	References
3P/PVC (3 : 3 : 3 : 1) 20 g	51.5 in PVC	–	–	430°C, N_2	890 mg (870 mg of HCl, 17 mg of chlorinated organic compounds)	[6]
3P/PVC/PET (3 : 3 : 3 : 1 : 1) 20 g	51.5 in PVC	–	–	430°C, N_2	812 mg (760 mg of HCl, 28 mg of chlorinated organic compounds)	[6]
MPW, 20 g	1.2in mixture	–	–	430°C, N_2	162 mg (57 mg of HCl, 52 mg of chlorinated organic compounds)	[6]
3P/PVDC (3 : 3 : 3 : 1), 10 g	73.2 PVDC	–	–	430°C, N_2	89% HCl, 10.8% chlorine in solid residue, 0.3% chlorinated organic compounds	[46]
3P/PVC (3 : 3 : 3 : 1) , 10 g	52.4 in PVC	–	–	430°C, N_2	96.5% HCl, 3.13% solids, 0.5% chlorinated organic compounds	[46]
3P/PVC (3 : 3 : 3 : 1) 20 g	51.5 in PVC	–	–	420°C, N_2	71% HCl, 23.6% chlorine in solid residue, 5.2% chlorinated organic compounds	[49]
3P/PVC (3 : 3 : 3 : 1) 20 g	51.5 in PVC	Al–Mg oxide	Mixture/ catalyst = 5/1	420°C, N_2	7.2% HCl, 91.4% solids, 1.4% chlorinated organic compounds	[49]
PE (40%)/PP (35%)/PS (18%)/ PET(4%)/PVC (3%) 100 g	1.1in mixture	–	–	500°C, stream N_2, 30 min	~100% (0.5% chlorine in oils, 0.3% chlorine in solid residue, 68% HCl, 31% chlorinated organic compounds)	[52]
PE (40%)/PP (35%)/PS (18%)/ PET (4%)/PVC (3%) 100 g	1.1in mixture	–	–	300°C, 120 min, stream N_2, 500°C	~100% (0.2% chlorine in oils, 0.2% chlorine in solid residue, 89% HCl, 10% chlorinated organic compounds)	[52]
PE (40%)/PP (35%)/PS (18%)/ PET (4%)/PVC (3%) 100 g	1.1in mixture	$CaCO_3$	Ca:Cl=3:1	500°C, stream N_2, 30 min	~100% (0.6% chlorine in oils, 6.7% chlorine in solid residue, 40% HCl, 28% chlorinated organic compounds)	[52]

Table 3. (Contd.)

Polymer/copolymer	Chlorine content, %	Additive	Substrate/additive	Conditions	Results	References
PE (40%)/PP (35%)/PS (18%)/PET (4%)/PVC (3%) 100 g	1.1in mixture	$CaCO_3$	Ca:Cl=3:1	300°C, 120 min, stream N_2, 500°C	~100% (0.2% chlorine in oils, 7.5% chlorine in solid residue, 50% HCl, 12% chlorinated organic compounds)	[52]
PE (40%)/PP (35%)/PS (18%)/PET (4%)/PVC (3%) 100 g	1.1in mixture	ZSM-5	10 g of catalyst/100 g of mixture	440°C, 500°C, stream N_2	500°C, ~100% (1.3% chlorine in oils, 0.1% chlorine in solid residue)	[53]
PE (40%)/PP (35%)/PS (18%)/PET (4%)/PVC (3%) 100 g	1.1in mixture	RedMud	10 g of catalyst/100 g of mixture	440°C, 500°C, stream N_2	500°C, ~100% (1.1% chlorine in oils, 3.7% chlorine in solid residue)	[53]
MPW 50 g	1.5in mixture	–	–	510–520°C, N_2	in gases 102202 ppm, in oil 4364 ppm, in residue 1950 ppm	[1]
MPW 50 g	1.5in mixture	Ni/ZSM-5/$Ca(OH)_2$/RedMud	2 g of catalyst/50 g of mixture	510–520°C, N_2	in gases 58128 ppm, in oil 284 ppm, in residue 45000 ppm	[1]
MPW 50 g	1.5in mixture	Ni/SAPO-11/$Ca(OH)_2$/RedMud	2 g of catalyst/50 g of mixture	510–520°C, N_2	in gases 43576 ppm, in oil 228 ppm, in residue 17000 ppm	[1]

Note: 3P/PVC, polypropylene/polystyrene/polyethylene/polyvinyl chloride; PET, poly(ethylene terephthalate); PP, polypropylene, PS, polystyrene, PE, polyethylene; PVDC, polyvinylidene chloride; and MPW, municipal plastics waste.

inorganic chlorine (Table 3). Larger amount of chlorine-containing compounds in the solid residue of municipal plastics waste (53 mg), compared to the fraction of chlorinated compounds formed by pyrolysis of the other mixtures, was due to the reaction of hydrogen chloride released from polyvinyl chloride with additives present in municipal plastics waste. Gas-chromatographic analysis of the liquid products revealed the presence of 2-chloro-2-phenylpropane, 2-chloro-2-methylpropane, 2-chloro-2-methylpentane, α-chloroethylbenzene, and chlorinated benzoic acid esters. The liquid products mainly consisted of hydrocarbons C_7–C_{10} (up to 45% in MPW, 40% in 3P/PVC/PET, and 20% in polyvinyl chloride), C_{13}–C_{15} (up to 10%), and C_{17}–C_{19} (up to 15%). The C_7–C_{10} hydrocarbons whose content was high in pyrolysis oils were monomers of the polymers present in the mixture.

The fraction of liquid products in the 3P/PVDC pyrolysis was 58% [46], which was somewhat lower compared to the fraction of oils in the 3P/PVC pyrolysis [6]. Similarly to the content of chlorinated organic compounds in liquid pyrolysis products formed from pure polyvinylidene chloride and polyvinyl chloride and from their binary mixtures, the content of chlorine-containing compounds in 3P/PVDC pyrolysis oils was lower than that in 3P/PVC oils: 0.3%, or 245 ppm.

Lopez et al. [52] studied the dechlorination of a plastic mixture containing 40% polyethylene, 35% polypropylene, 18% polystyrene, 4% poly(ethylene terephthalate), and 3% polyvinyl chloride (composition close to that of municipal plastics waste) by pyrolysis in a nitrogen stream on the semicommercial scale (m = 100 g). The stepwise pyrolysis (275–500°C) of the mixture yielded a smaller fraction of oils, 58.2–61.7% depending on the temperature (275–300°C) and duration (30–120 min) of the first step, compared to the common pyrolysis (65.2%), whereas the fraction of gases and solid residue increased. Aromatic compounds in oils in stepwise pyrolysis were formed in a 15% smaller amount than in common pyrolysis. Stepwise pyrolysis of the polymer mixture allowed the content of chlorinated compounds to be decreased to 0.2% in oils and to 0.1–0.2% in the solid residue against 0.5 and 0.3%, respectively, in common pyrolysis, whereas the fraction of gaseous HCl increased from 2.2 to 2.5%.

The catalyst was used for accelerating the dechlorination and the subsequent cracking of the hydrocarbons formed, and the sorbents were used for increasing the degree of binding of gaseous HCl, thus decreasing the content of chlorine-containing compounds in pyrolysis oils. The solid residue from pyrolysis contained permissible amount of chlorinated organic compounds [18] and could be used as a solid fuel.

The use of the Al–Mg composite [49] as a catalyst and sorbent in pyrolysis of 3P/PVC, as in pyrolysis of binary mixtures, led to a significant decrease in the content of chlorinated organic compounds in pyrolysis oils (from 8100 to 1900 ppm) and of gaseous chlorine due to absorption by MgO.

Addition of the $CaCO_3$ sorbent in pyrolysis of a plastics mixture containing 40% polyethylene, 35% polypropylene, 18% polystyrene, 4% poly(ethylene terephthalate), and 3% polyvinyl chloride [52], like the use of Al–Mg in [49], led to a decrease in the fraction of chlorinated compounds in the liquid (25%) and gas (40%) phases due to absorption of the hydrogen chloride released from polyvinyl chloride. The formation of a larger amount of C_5–C_9 compounds such as styrene, toluene, etc., in the presence of $CaCO_3$ may be due to the catalytic properties of $CaCO_3$ itself. Larger volume of gases in the products, compared to the pyrolysis without $CaCO_3$, was probably due to deeper cracking as a result of the reaction of the released HCl with the $CaCO_3$ sorbent. The major components of the solid pyrolysis products were semicoke with high calorific value, which could become an alternative to fossil fuel, and also $CaCO_3$ and $CaCl_2$. The fraction of chlorinated organic compounds upon stepwise pyrolysis over $CaCO_3$ did not exceed 0.2% in pyrolysis liquids, 1.7% in the gases, and 7.5% in the solid residues.

Catalytic pyrolysis of a mixture of polymer wastes described in [52], containing 1.1 at. % Cl, was performed in the presence of ZSM-5 and RedMud in [53]. As expected, at a higher temperature (500°C), the fraction of liquid oils decreased and the fraction of gases increased owing to deeper cracking.

Because of high porosity and acidity of ZSM-5 zeolite, its addition favored the degradation of polymer components, leading to an increase in the fraction of liquid products compared to the noncatalytic process. The presence of a large number of Brønsted acid sites in the zeolite structure favored the aromatization and acceleration of coking reactions leading to rapid deactivation of the catalyst already after the first cycle. In contrast to the zeolite, RedMud influenced the distribution of the pyrolysis products insignificantly.

The fraction of chlorine-containing compounds in the pyrolysis oil was 0.2 and 0.5% after the heat treatment at 440 and 500°C, respectively. With zeolite, this fraction increased to 1.2 and 1.3%, and with RedMud, to 0.5 and 1.1%, respectively. This may be due to high cracking power of catalysts with the generation of alkyl radicals, which, in turn, reacted with HCl released in the course of polyvinyl chloride degradation in the mixture.

The absence of hydrogen chloride in the gaseous products is caused by its reaction with active sites of the catalysts (ZSM-5 and RedMud). High fraction of chlorinated compounds in the solid residue over RedMud (3.7–4.2%), compared to the content of chlorinated organic compounds in the semicoke from the noncatalytic pyrolysis (less than 0.1%) or pyrolysis over zeolite (0.1%), was due to the reaction of metal oxides as catalyst components with the released HCl to form the corresponding chlorides.

Fekhar et al. [1] studied the effect of the catalytic mixtures Ni/ZSM-5, RedMud, $Ca(OH)_2$, and Ni/SAPO-11 on the composition of products formed by pyrolysis of municipal plastics waste consisting of 35% low-density polyethylene, 32% high-density polyethylene, 24% polypropylene, 4% polyvinyl chloride, 3% ethylene–propylene dimer, and 2% polystyrene. In the course of pyrolysis, hydrocarbon macromolecules penetrate into the catalyst pores where additional cleavage of the C–C bond occurs. The SAPO-11 support, compared to ZSM-5, has slightly larger mean pore diameter. Therefore, coarser molecules of size exceeding the pore size did not underwent additional cleavage. The molecules with a long carbon chain, when reaching active sites, underwent cyclization and polycyclization to form coke, which, in turn, deactivated the catalyst. Therefore, the amount of solid products (including coke) formed on catalysts on the SAPO-11 support was larger compared to the ZSM-5 support.

The addition of catalysts to the reaction mixture led to extensive isomerization of gaseous products. The gases obtained over Ni/ZSM-5 and Ni/SAPO-11/$Ca(OH)_2$/RedMud contained up to 51.2–56.1 and 47.7–58.6% branched hydrocarbons, respectively. A decrease in the fraction of branched hydrocarbons in the second case was due to the addition of $Ca(OH)_2$ to the catalytic mixture.

The pyrolysis oils were mixtures of C_5–C_{30} hydrocarbons: linear olefins, paraffins, and branched and aromatic hydrocarbons. When using the catalysts, the fraction of aromatic and unsaturated hydrocarbons in pyrolysis oils considerably increased owing to cyclization of hydrocarbon molecules in pores and on the catalyst surface near the active sites.

The content of chlorinated organic compounds in gaseous products of noncatalytic pyrolysis, in pyrolysis oil, and in the residue was 102 202, 4364, and 1950 ppm, respectively.

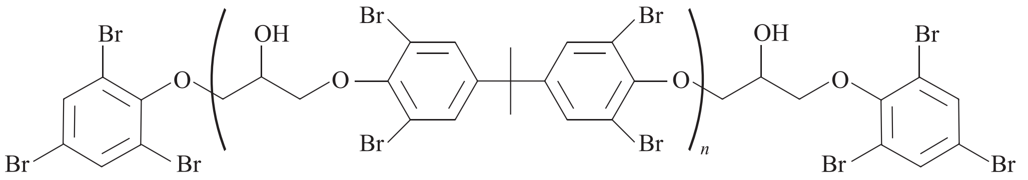
The concentration of chlorinated organic compounds in pyrolysis oil obtained in the presence of Ni/ZSM-5, compared to Ni/SAPO-11, decreased (to 500 ppm) owing to the formation of a larger amount of hydrogen in the gaseous products with its easy binding with chlorine radicals to form HCl (up to 70 000 ppm). On adding a mixture of $Ca(OH)_2$ and RedMud, the content of chlorinated compounds in pyrolysis oil considerably decreased in both cases: to 284 ppm over Ni/ZSM-5/$Ca(OH)_2$/RedMud and to 228 ppm over Ni/SAPO-11/$Ca(OH)_2$/RedMud. The use of the catalysts decreased the yield of gaseous hydrogen chloride by half.

Bhaskar et al. [6] demonstrated by the example of the pyrolysis of model mixtures containing various polymers and of municipal plastics waste that the presence of poly(ethylene terephthalate), plasticizers, and stabilizers (components of municipal plastic waste) in the model mixtures favored an increase in the fraction of chlorinated hydrocarbons in the oils. A stepwise increase in the pyrolysis temperature in semicommercial experiments performed in [52] in a nitrogen stream with a mixture similar in the composition to municipal plastics waste, compared to common pyrolysis, led to a decrease in the fraction of chlorinated organic compounds by 21% due to an increase in the content of gaseous hydrogen chloride. In catalytic pyrolysis [52, 53], $CaCO_3$ proved to be a more effective additive than RedMud, and the addition of ZSM-5 zeolite favoring the degradation with the subsequent increase in the fraction of liquid oils led to more extensive formation of chlorinated compounds. As in the noncatalytic process, stepwise pyrolysis in the presence of $CaCO_3$ improved the quality of pyrolysis oils: 0.2% chlorinated organic compounds compared to 0.6% in common pyrolysis. Simultaneous use of different catalysts and sorbents in pyrolysis of municipal plastics waste [1] revealed higher performance of Ni/SAPO-11 zeolite in combination with $Ca(OH)_2$ and RedMud: Due to sorption, the fraction of gaseous hydrogen chloride decreased by a factor of 2 compared to the noncatalytic pyrolysis of municipal plastics waste, and the content of chlorinated organic compounds in the liquid products was as low as 228 ppm.

Pyrolysis of bromine-containing waste in a mixture with polyvinyl chloride. Because some kinds of municipal plastics waste contain up to 4% brominated acrylonitrile–butadiene–ethylene–styrene copolymer (ABS-Br) [6, 54], which is a component of many electronic and sensor devices, the mutual effect of chlorine- and bromine-containing compounds on the overall waste pyrolysis in the course of waste recycling is a topical problem.

Brebu et al. [41] studied the effect of polyvinyl chloride and/or poly(ethylene terephthalate) additions on the noncatalytic pyrolysis of a 3P/ABS-Br mixture, in which ABS-Br contained brominated flame retardant [55] and antimony oxide. In contrast to pure acrylonitrile–butadiene–ethylene–styrene copolymer, the degradation of brominated acrylonitrile–butadiene–ethylene–styrene copolymer occurs in two steps: release of the brominated flame retardant at 320–425°C and degradation of the copolymer to the monomers at 470–520°C with the formation of 10 wt % solid residue consisting of compounds obtained by internal cyclization of acrylonitrile units in the copolymer. The major inorganic gases released in the course of the polymer degradation are NH_3, HCN, HCl, and HBr.

Structure of the brominated epoxy resin oligomer with terminal tribromophenol groups (derived from 2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol diglycidyl ether)



The pyrolysis of 3P/ABS-Br led to the formation of 11 wt % gaseous product, 13 wt % solid residue, and 73 wt % oils. The addition of polyvinyl chloride and/or poly(ethylene terephthalate) favored a decrease in the fraction of oils (to 52% with both polymers added) and an increase in the fraction of gaseous products (to 22% with both polymers added). Addition of polyvinyl chloride to the mixture led to an increase in the formation of paraffin hydrocarbons and to a decrease in the solid residue. The mean number of carbon atoms in the oils varied from 9.4 to 9.8. The degradation of the 3P/ABS-Br/PVC/PET mixture occurred within only 2 h, whereas the 3P/ABS-Br mixture without polymer additives degraded within 4 h; i.e., the presence of polyvinyl chloride and/or poly(ethylene terephthalate) considerably accelerated the degradation owing to a decrease in the temperatures at which the polymer weight loss reached a maximum.

Thermal degradation of polyethylene yields a wide range of linear saturated and unsaturated hydrocarbons and small amounts of aromatic compounds, that of polypropylene yields branched and aromatic hydrocarbons, and that of polystyrene yields mainly styrene and other benzene derivatives. The presence of polyvinyl chloride and poly(ethylene terephthalate) in the 3P/ABS-Br mixture favored a decrease in the amount of heavy C_{13}–C_{17} compounds formed in the course of polyethylene and polypropylene degradation due to their conversion to light C_5–C_8 compounds.

Separate addition of polyvinyl chloride or poly(ethylene terephthalate) to a 3P/ABS-Br mixture did not noticeably influence the amount of nitrogen-containing compounds formed by degradation or reaction of acrylonitrile present in the brominated acrylonitrile–butadiene–ethylene–styrene copolymer with other components of the polymers (Table 4), whereas the presence of both additives led to a considerable decrease in this fraction to 355 ppm.

The presence of polyvinyl chloride or poly(ethylene terephthalate) in 3P/ABS-Br led to an increase in the fraction of brominated compounds by a factor of 2–2.5 compared to the pyrolysis of the straight 3P/ABS-Br mixture due not only to a change in the nitrile ratio, but also to the reaction of degradation products of polyvinyl chloride, poly(ethylene terephthalate), and brominated flame retardant in acrylonitrile–butadiene–ethylene–styrene copolymer, causing the formation of brominated compounds in pyrolysis oils [55]. The addition of poly(ethylene terephthalate) to 3P/ABS-Br/PVC led to an increase in the concentration of chlorinated

Table 4. Conditions of pyrolysis of bromine-containing wastes in a mixture with polyvinyl chloride

Polymer/copolymer	Cl, Br content, %	Additive	Substrate/additive	Conditrions	Results	References
3P/ABC-Br (3:3:3:1), 10 g	56.7 in PVC, 9.3 in ABC-Br	–	–	450°C, N_2	N 1071 ppm Br 1228 ppm Cl 0 ppm	[41, 55]
3P/ABC-Br/PVC (3:3:2:1:1), 10 g	56.7 in PVC, 9.3 in ABC-Br	–	–	450°C, N_2	N 1170 ppm Br 1924 ppm Cl 4972 ppm	[41, 55]
3P/ABC-Br/PVC/PET (3:3:2:1:0.5:1:0.5), 10 g	56.7 in PVC, 9.3 in ABC-Br	–	–	450°C, N_2	N 355 ppm Br 2730 ppm Cl 5254 ppm	[41, 55]
3P/ABC-Br/PVC (3:3:2:1:1), 10 g	56.7 in PVC, 9.3 in ABC-Br	FeOOH	10 g mixture/2 g catalyst	450°C, N_2, vapor phase	N 840 ppm Br 104 ppm Cl 3370 ppm	[56]
3P/ABC-Br/PVC (3:3:2:1:1), 10 g	56.7 in PVC, 9.3 in ABC-Br	Fe/C	10 g mixture/2 g catalyst	450°C, N_2 vapor phase	N 981 ppm Br 170 ppm Cl 1014 ppm	[56]
3P/ABC-Br/PVC (3:3:2:1:1), 10 g	56.7 in PVC, 9.3 in ABC-Br	Ca/C	10 g mixture/2 g catalyst	450°C, N_2 vapor phase	N 1370 ppm Br 418 ppm Cl 113 ppm	[56]
3P/ABC-Br/PVC (3:3:2:1:1), 10 g	56.7 in PVC, 9.3 in ABC-Br	$CaCO_3$	10 g mixture/2 g catalyst	450°C, N_2 vapor phase	N 1078 ppm Br 1161 ppm Cl 355 ppm	[56]
3P/PVC/PS-Br (3:3:2:1:1), 10 g	56.7 in PVC, 10.8 in PS-Br	–	–	430°C, N_2	Br 7330 ppm Cl 1120 ppm	[58]
3P/PVC/PS-Br (3:3:2:1:1), 10 g	56.7 in PVC, 10.8 in PS-Br	Ca/C	10 g mixture/4 g catalyst	430°C, N_2	Br 0 ppm Cl 0 ppm	[58]
3P/PVC/PET/PS-Br (3:3:2:1:0.5:0.5), 10 g	56.7 in PVC, 10.8 in PS-Br	–	–	430°C, N_2	Br 4900 ppm Cl 2850 ppm	[58]
3P/PVC/PET/PS-Br (3:3:2:1:0.5:0.5), 10 g	56.7 in PVC, 10.8 in PS-Br	Ca/C	10 g mixture/8 g catalyst	430°C, N_2	Br 300 ppm Cl 20 ppm	[58]

Note: 3P, mixture of polypropylene, polyethylene, and polystyrene; ABS-Br, brominated acrylonitrile–butadiene–ethylene–styrene copolymer; PVC, polyvinyl chloride; PET, poly(ethylene terephthalate); PS-Br, brominated polystyrene.

organic compounds in the oil due to formation of heavy hydrocarbons C_{15}–C_{16} and C_{18}–C_{21} [55].

Catalytic pyrolysis of the 3P/ABS-Br/PVC mixture was performed in the vapor-phase contact mode. Catalysts based on iron (FeOOH and Fe/C) and calcium ($CaCO_3$ and Ca/C) were compared [56]. Noncatalytic pyrolysis of the mixture yielded 59 wt % liquid products [41]; the mean number of carbon atoms in them was 9.6. The use of catalysts led to an increase in the liquid product fraction to 63–67 wt % and in its density due to the formation of condensed compounds. The major components of the oils were the monomers of the mixture polymers and their derivatives.

Iron-containing catalysts [57] in the course of debromination of the brominated acrylonitrile–butadiene–ethylene–styrene copolymer showed higher performance in removal of bromine atoms (up to 90%), whereas calcium catalysts were more effective in the removal of chlorine atoms (93–98%); both types of the catalysts reduced the content of nitrogen-containing compounds in the products insignificantly. For example, the degree of debromination decreased in the order FeOOH > Fe/C > Ca/C > $CaCO_3$, and the degree of dechlorination, in the order Ca/C > $CaCO_3$ > Fe/C > FeOOH. Lower degree of dechlorination of pyrolysis oil in the presence of FeOOH (30%) compared to Fe/C (80%) was caused by the structure of the catalyst, which in the course of catalytic degradation transformed into $Fe_2O_3 \cdot nH_2O$, Fe_2O_3, and finally Fe_3O_4. Fe_2O_3 acting as a dechlorination catalyst and chlorine sorbent in the course of polyvinyl chloride degradation transformed into the hydrates $FeCl_2 \cdot 2H_2O$ and $FeCl_2 \cdot 4H_2O$, which, in turn, favored the formation of chlorinated compounds from hydrocarbons formed by thermal degradation of polyolefins in the mixture.

Bhaskar et al. [58] studied the effect of brominated polystyrene (PS-Br) on the pyrolysis of the 3P/PVC and 3P/PVC/PET mixtures in the presence of the Ca/C composite. As in [6, 41], the addition of poly(ethylene terephthalate) to the 3P/PVC/PS-Br mixture increased not only the amount of chlorinated organic compounds in pyrolysis oils but also the fraction of gaseous products and solid carbon residues and decreased the fraction of the liquid to 60–66% compared to the thermal degradation of 3P/PVC/PS-Br (up to 71% oils).

The major chlorinated products were branched alkanes (C_4, C_6, C_8) formed by the reaction of HCl released in the course of the polyvinyl chloride pyrolysis with polypropylene degradation products. Tertiary carbon atoms of polypropylene degradation products, owing to the lability of the hydrogen atoms at such carbon atoms, are more reactive toward Cl atoms than secondary carbon atoms of n-alkenes and n-alkadienes, which are the major unsaturated products of polyethylene degradation. HCl also reacted with the styrene monomer and dimer to form a large amount of 1-chloroethylbenzene and chlorinated diphenylbutane and pentane. Hydrogen bromide formed by thermal pyrolysis reacted mainly with branched alkenes and styrene. The yield of chlorinated branched alkanes increased in the presence of poly(ethylene terephthalate). The formation of brominated alkenylbenzenes was due to the reaction of polystyrene and polypropylene degradation products with HBr, and the formation of vinyl bromide and ethyl bromide, to bromination of the ethylene segments of poly(ethylene terephthalate).

The Ca/C composite catalyst, as in [56], showed 100% efficiency of the dechlorination and debromination of the 3P/PVC/PS-Br mixture in the course of its pyrolysis: 0 ppm brominated and chlorinated organic compounds, in contrast to 1120 ppm chlorinated and 7330 ppm brominated compounds in thermal pyrolysis.

The addition of poly(ethylene terephthalate) to the polymer mixture considerably decreased the degree of dechlorination. Only a twofold increase in the weight of the Ca/C catalyst in pyrolysis of 3P/PVC/PET/PS-Br compared to the pyrolysis of 3P/PVC/PS-Br allowed removal of 94% of Br (residual content 300 ppm) and more than 99% of Cl (residual content 20 ppm).

The addition of brominated acrylonitrile–butadiene–ethylene–styrene copolymer and polystyrene to the 3P/PVC mixture considerably increased the amount of chlorinated organic compounds due to the reaction of the released HCl with the brominated flame retardant and degradation products of the other polymers [41, 58]. As in the previous study [6], the presence of poly(ethylene terephthalate) also increased the fraction of chlorinated organic compounds in the oils by 300 ppm in the case of the mixture with brominated acrylonitrile–butadiene–ethylene–styrene copolymer [41] and by 1700 ppm in the case of the mixture with brominated polystyrene [58]. The Ca/C composite showed the highest performance in the dechlorination of the mixture containing brominated acrylonitrile–butadiene–ethylene–styrene copolymer and polyvinyl chloride, whereas FeOOH showed good ability to take up bromine [41]. The addition of

Table 5. Conditions of joint pyrolysis of polyvinyl chloride waste with biomass

Substrate	Chlorine content, %	Conditions	Results	References
Pine wood 8 mg	–	600°C, stream N_2	Fractions: oil 19.1%, coal 20.1%; H/C = 1.3, O/C = 0.15 in oil; fraction of aromatics: 0 rings 34.8%, 1 ring 63.3%, two rings 1.9%	[59]
Pine wood/PVC (3:1) 8 mg	56.1 in PVC	600°C, stream N_2	Fractions: oil 17.5%, coal 19.5%; H/C = 0.87, O/C = 0.08 in oil; fraction of aromatics: 1 ring 5.8%, 2 rings 63.5%, 3 rings 18.7%	[59]
Pine wood/PVC (1:1) 8 mg	56.1 in PVC	600°C, stream N_2	Fractions: oil 16.8%, coal 16%; H/C = 0.83, O/C = 0.04 in oil; fraction of aromatics: 1 ring 9%, 2 rings 61.2%, 3 rings 20.6%	[59]
Pine wood/PVC (1:3) 8 mg	56.1 in PVC	600°C, stream N_2	Fractions: oil 15.6%, coal 14.5%; H/C = 0.83, O/C = 0.02 in oil; fraction of aromatics: 1 ring 13.7%, 2 rings 55.6%, 3 rings 21.1%	[59]
PVC 8 mg	56.1 in PVC	600°C, stream N_2	Fractions: oil 18.1%, coal 7.9%; H/C = 0.82, O/C = 0 in oil; fraction of aromatics: 1 ring 21.2%, 2 rings 46.6%, 3 rings 21%	[59]
Pine sawdust/10 wt % PVC 5 mg	49.4 in PVC, 0.2 in pine sawdust	997°C, N_2/CO_2 = 100%/0%, 3/1, 1/1, 1/3, 0%/100%	–	[60]
Paper/10 wt % PVC 5 mg	49.4 in PVC		–	[60]
PVC, 10 g		500°C, N_2	Fractions: oil 16.1%, gases 83.0%	[61]
Walnut shells, 10 g	0.126	500°C, N_2	Fractions: oil 20.8%, coke 30.6%; fractions in oil: aromatics 22.8%, phenol 58.5%; H/C = 1.3, O/C = 0.35 in oil (24.4 MJ kg^{-1}); H/C = 0.69, O/C = 0.18 in solid residue (28.9 MJ kg^{-1})	[61]
Walnut shells/PVC (1 : 1), 10 g	46.37 in PVC, 0.126 in CO	500°C, N_2	Fractions: oil 17.6%, coke 20%; fraction of PAHs in oil 64.4%; H/C = 1.08, O/C = 0.03 in oil (40.5 MJ kg^{-1}); H/C = 0.51, O/C = 0.11 in solid residue (31.3 MJ kg^{-1})	[61]
Peach stones, 10 g	–	500°C, N_2	Fractions: oil 18.3%, coke 33.6%; fractions in oil: aromatics 23.7%, phenol 49.2%; H/C = 1.23, O/C = 0.37 in oil (24.7 MJ kg^{-1}); H/C = 0.54, O/C = 0.13 in solid residue (30.3 MJ kg^{-1})	[61]
Peach stones/PVC (1 : 1), 10 g	46.37 in PVC	500°C, N_2	Fractions: oil 14.7%, coke 20.3%; fraction of PAHs in oil 59.1%; H/C = 1.06, O/C = 0.06 in oil (38.7 MJ kg^{-1}); H/C = 0.49, O/C = 0.09 in solid residue (32.1 MJ kg^{-1})	[61]

Table 5. (Contd.)

Substrate	Chlorine content, %	Conditions	Results	References
Soybean protein, 10 mg		400–600°C, stream N_2	Tar fraction 7.8 (400°C)–8.8% (600°C) Coke fraction 26.6 (400°C)–22.2% (600°C)	[62]
Soybean protein/PVC waste (4 : 1) 10 mg	53.2 in PVC waste	400–600°C, stream N_2	Tar fraction 7.5%, coke fraction 24.5%, PAHs in tar 65% (600°C)	[62]
Soybean protein/PVC waste (1 : 1) 10 mg	53.2 in PVC waste	400–600°C, stream N_2	Tar fraction 6.2%, coke fraction 18%, PAHs in tar 78% (600°C)	[62]
Soybean protein/PVC waste (1 : 4) 10 mg	53.2 in PVC waste	400–600°C, stream N_2	Tar fraction 4.2%, coke fraction 12%, PAHs in tar 80% (600°C)	[62]
PVC 10 mg	53.2 in PVC waste	400–600°C, stream N_2	Tar fraction 9.5 (400°C)–7.2% (600°C), coke fraction 11.8 (400°C)–6.6% (600°C)	[62]
marine algae *Enteromorpha clathrata*	3.2	550°C, stream N_2	Fractions: oil 44.8%, coke 41.7% (H/C = 0.81), noncondensable gas 13.5%, aromatic compounds in oil 3.4%, phenols in oil 20%	[63]
Algae/PVC (5–25 wt %)	3.2 in algae, 47.7 in PVC	550°C, stream N_2	Fractions: oil 43.5%, coke 41.2% (H/C = 0.71), noncondensable gas 15.3%, aromatic compounds in oil 12.7%, phenols in oil 30%	[63]
Algae /PVC (5–25 wt %)	3.2 in algae, 47.7 in PVC	550°C, stream N_2	Fractions: oil 38.2%, coke 37.7% (H/C = 0.60), noncondensable gas 24.2%, aromatic compounds in oil 25.4%, phenols in oil 35%	[63]
PVC	47.7	550°C, stream N_2	Fractions: gas 96.4%, coke 3.4% (H/C = 0.56), aromatic compounds in oil 95.4%, phenols in oil 0%	[63]
Lignin/PVC (1 : 1), 10 g	56.1 in PVC	750°C, N_2, 4 h	Biocoal fraction before washing 29%, S_{BET} = 101 $m^2 g^{-1}$, sorption 0.1 mg g^{-1}	[65]
Lignin/PVC/KOH, 10 g (1 : 1)/10 g KOH	56.1 in PVC	750°C, N_2, 4 h	Biocoal fraction before washing 55%, after washing 4%, S_{BET} = 1513 $m^2 g^{-1}$, sorption 263.4 mg g^{-1}	[65]
Rice hulls/PVC, 10 g (1 : 1)	56.1 in PVC	750°C, N_2, 4 h	Biocoal fraction before washing 26%, S_{BET} = 253 $m^2 g^{-1}$, sorption 0.1 mg g^{-1}	[65]
Rice hulls/PVC/KOH, 10 g (1 : 1)/10 g KOH	56.1 in PVC	750°C, N_2, 4 h	Biocoal fraction before washing 52%, after washing 3%, S_{BET} = 879 $m^2 g^{-1}$, sorption 82.8 mg g^{-1}	[65]
Paper/PVC (10 : 0, 3 : 1, 9 : 1) 1.6 g	58.5 in PVC	600–800°C, stream N_2	700°C, 3 : 1, coal yield 37.5%, chlorine fraction in biocoal 1.55%, S_{BET} = 10.7 $m^2 g^{-1}$, sorption 82.8 mg g^{-1}	[66]

a larger amount of the Ca/C catalyst to the 3P/PVC/PS-Br reaction mixture allowed complete removal of both chlorinated and brominated compounds formed by degradation of the polymer mixture components [58].

Joint pyrolysis of polyvinyl chloride waste and biomass. Joint (so-called “green”) recycling of biological and plastics wastes has become recently a topical line in waste recycling [59–68]. Joint recycling of polyvinyl chloride and biomass allows an increase in the fraction of liquid products and improvement of the quality of pyrolysis oils and solid residue due to binding and removal of chlorinated compounds with biomass components [59–67]. The major product of the joint pyrolysis is semicoke with relatively high calorific value, allowing its use as a solid fuel along with brown coal and bitumen [64]. In the course of joint pyrolysis of biomass and polyvinyl chloride with various additives, some researchers obtained biocoal exhibiting relatively high sorption ability to remove, e.g., toluene [65] and mercury [66, 67] from wastewater.

The pyrolysis should be performed in an inert atmosphere, because in the presence of oxygen side reactions yielding toxic dioxins, benzofurans, etc. are possible [38]. Lu et al. [59] studied the pyrolysis of a mixture of biomass (pine wood) and polyvinyl chloride. The weight loss rate in pyrolysis of pure pine wood passed through a maximum at 350°C, and the main weight loss occurred in the temperature interval 250–380°C. This weight loss can be attributed to the dehydration and formation of free radicals, oxygenated compounds, and carbonaceous residues. The mixture of the biomass with polyvinyl chloride degrades in two steps. The first step (200–400°C) involves dehydrochlorination of polyvinyl chloride and degradation of hemicellulose and cellulose, and the second step (400–500°C) involves degradation of dechlorinated polyvinyl chloride and lignin. The temperature corresponding to the weight loss maximum appreciably decreased (by 47–51°C) owing to the interaction of wood with polyvinyl chloride.

The pyrolysis of cellulose, which is the major component of the biomass, involves two competing reactions: (1) dehydration and charring and (2) transglycosylation and formation of levoglucosan. The HCl released from polyvinyl chloride at relatively low temperatures (230–300°C) favors the cellulose dehydration and formation of aldehyde from cellulose, which decreased the depolymerization rate and the yield of pyrolysis oils. Thus, on adding wood to polyvinyl chloride, the semicoke yield increased by 15.5–27.9% with an increase in the fraction of the polymer in the mixture, and the yield of oils correspondingly decreased by 7.2–14.4% (Table 5).

As compared to the content of carbon and hydrogen atoms in the coal formed by pyrolysis of pine wood, on adding polyvinyl chloride and with increasing its content the fraction of carbon atoms increased and that of hydrogen atoms, correspondingly, slightly decreased. Low H/C atomic ratio (0.38) means that the semicoke mainly consists of fixed aromatic carbon rings. The fraction of the C and H atoms in the pyrolysis oil obtained from a mixture of the biomass with the polymer changed similarly, with a decrease in the H/C ratio (to 0.83). With the addition of the polymer to a mixture with wood, the content of aromatic compounds, mainly with two or three rings, increased, and the fraction of oxygen-containing compounds in pyrolysis oils decreased, which improved the properties of pyrolysis oils for their use as a fuel.

Similar pattern was observed in pyrolysis of a mixture of biomass (pine sawdust and paper) with polyvinyl chloride (10 wt %) [60]. The pine sawdust mainly consisted of cellulose (45–50 wt %), hemicellulose (27–39 wt %), and lignin (21–30 wt %); the major component of paper, as a rule, was cellulose (more than 70 wt %).

As in [59], the addition of 10 wt % polyvinyl chloride to the biomass favored a decrease in the temperature corresponding to the weight loss maximum by 30°C and acceleration of the polyvinyl chloride dehydrochlorination, irrespective of the kind of the biomass and the atmosphere in which the process was performed [60]. The biomass degradation accelerated at lower temperatures in the presence of the polymer, which was due to possible catalytic effect of the gaseous HCl released from polyvinyl chloride at 250–350°C. Hydrogen chloride as an acid favored the biomass degradation with the formation of aldehyde and the decarbonylation and decarboxylation, leading to an increase in the amount of solid carbonaceous residues.

An increase in the CO_2 fraction influenced the biomass degradation at temperatures lower than 773°C insignificantly, but accelerated the process at higher temperatures owing to gasification of the charcoal (major component of the solid residue) and carbon:

$$C_mH_nO + CO_2 \rightarrow CO + H_2O,$$
$$C + CO_2 \rightarrow 2CO + 173.5\ \text{kJ mol}^{-1}.$$

Ozsin and Pütün [61] studied the joint pyrolysis of biomass waste (walnut shells and peach stones) and polyvinyl chloride. Thermal degradation of walnut shells and peach stones containing 26 and 36.9% lignin occurred with three main steps of the weight loss: loss of bound moisture (22–175°C), active pyrolysis (180–480°C), and passive pyrolysis due to secondary degradation (>700°C). After the completion of active pyrolysis, the walnut shell biomass lost 61.4% of its initial weight, and the peach stone biomass lost 59.8%. The addition of biomass in pyrolysis of polymers slightly decreased the temperature of the weight loss maximum (to 270°C in the case of polyvinyl chloride).

In pyrolysis of the biomass, the highest biooil yield was reached at 500°C in both cases. Further increase in temperature led to a decrease in the yield of biooil and coke and to an increase in the fraction of gases, which was caused by deep cracking at high temperatures. The formation of a larger amount of coke in pyrolysis of peach stones was associated with higher lignin content of this material, compared to walnut shells.

The addition of biomass to polyvinyl chloride led to a decrease in the biomass fraction due to the formation of water and coke, compared to the pyrolysis of the pure biomass (Table 5). The major components of oils from walnut shells and peach stones are aromatic compounds, phenol, and its derivatives formed by degradation of the natural polymer, lignin. The formation of heavier aromatic compounds such as polycyclic aromatic hydrocarbons in joint pyrolysis of polyvinyl chloride and biomass was associated with the release of HCl, accompanying the internal cyclization and aromatization.

As in [59], the addition of polyvinyl chloride to the biomass led to changes in the content of carbon, oxygen, and hydrogen atoms in the pyrolysis oil and solid residue [61]; in this case, the calorific value of both the oils and the solid residue substantially increased.

Tang et al. [62] studied the joint pyrolysis of organic (soybean protein) and polyvinyl chloride wastes. Slight weight loss in soybean protein degradation is observed already at 200°C, suggesting the release of water, which continues up to 350°C. At higher temperatures, the polymer structure itself starts to degrade via bond cleavage, dehydration, and formation of free radicals, oxygen-containing compounds, and then carbonaceous residues (about 20 wt %) up to 530°C. In polyvinyl chloride pyrolysis (530°C), the weight of the residue is 4% of the initial weight.

Mixing of biomass with polyvinyl chloride waste favored a decrease in the temperatures of the weight loss onset and maximum and acceleration of the degradation due to HCl released from polyvinyl chloride. Similarly to the results of [59–61], the hydrogen chloride formed by the polyvinyl chloride degradation acts as an acid catalyst [62].

An increase in the pyrolysis temperature from 400 to 600°C led first to an increase in the yield of the tar in the case of the pure biomass and biomass/polyvinyl chloride (4 : 1 and 1 : 4) mixture and then to a decrease in the tar content. In the case of the 1 : 1 biomass/polyvinyl chloride mixture and polyvinyl chloride waste, the fraction of the formed tar decreased. The coke yield decreased with increasing temperature in all the cases. This may be due to the catalytic effect of HCl, which also suppressed the depolymerization and decreased the dehydration and charring rates. The tar obtained by the soybean protein pyrolysis contained hydrocarbons with 0–2 benzene rings, whereas the pyrolysis tar formed from polyvinyl chloride contained hydrocarbons with 0–3 benzene rings [59]. In pyrolysis of mixtures of the biomass with polyvinyl chloride waste at all the weight ratios of the components, the fraction of compounds containing two or three rings increased with temperature, and polycyclic aromatic hydrocarbons with four benzene rings appeared; i.e., the interaction of soybean protein with polyvinyl chloride in the course of joint pyrolysis considerably favored the formation of heavier components and the suppression of the formation of nitrogen-containing compounds except indole.

Thus, the addition of biomass to waste containing polyvinyl chloride favored complete removal of chlorinated compounds from the pyrolysis oils and solid residue, which confirms 100% efficiency of the joint pyrolysis of the polymer waste with biomass.

Cao et al. [63] studied the synergistic effect on the properties of the biomass and biocoal in joint pyrolysis of *Enteromorpha clathrate* macroalgae in a mixture with different gravimetric content of polyvinyl chloride (5–25 wt %). As in [59], the mixture degraded in two steps: dehydrochlorination of polyvinyl chloride and degradation of proteins and carbohydrates of the algae in the first step and degradation of dechlorinated polyvinyl chloride in the second step. With an increase in the polyvinyl chloride fraction in the mixture, the peaks of the maximal weight loss, in contrast to [59], were shifted toward higher temperatures owing to the catalytic properties of the HCl released from polyvinyl chloride, which interacts with algal degradation products.

The biooil obtained from the algae consists of oxygen- (alcohols, ketones, phenols, organic acids) and nitrogen-containing compounds (amines, amides, nitriles, pyridines) (55 and 20%, respectively) formed in the course of degradation of carbohydrates, proteins, and lipids present in the algae. On adding polyvinyl chloride, the yields of the biooil and biocoal decreased, whereas the fraction of the noncondensed gases proportionally increased. An increase in the fraction of polyvinyl chloride in the mixture led to the formation of decreased amounts of oxygen- (down to 15%) and nitrogen-containing (down to 4.6%) compounds in the oils, compared to the biooil from the algae, at the expense of increasing content of aromatic (up to 25%) and aliphatic (27.2%) hydrocarbons. The interaction of the algae and polyvinyl chloride in the course of the pyrolysis led to a decrease in the H/C ratio in the biocoal to 0.6, whereas in the biocoal obtained from macroalgae this ratio was 0.81, because HCl accelerated the algae dehydration, decreasing the hydrogen content.

The distribution of the Cl atoms in the biooil, biocoal, and noncondensable gas formed in the course of the algae pyrolysis was 5.1, 8.5, and 86.4%, whereas on adding polyvinyl chloride (to 25 wt % content) these values changed to 7.6, 77.1, and 15.3%, respectively; i.e., the major fraction of chlorinated compounds obtained from the mixture of algae with polyvinyl chloride was found in the biocoal and biooil owing to interaction of the substrates.

The addition of various activators in the course of the joint pyrolysis of the biomass and polyvinyl chloride favored the formation of biocoal, which can be used as a sorbent with relatively high surface area. For example, the addition of KOH, which is the most widely used activator, leads to the formation of more thermally stable biocoal, because its maximal porosity is reached at 700–900°C [65]. In the course of carbonization in the presence of KOH, the K_2CO_3 formed in situ influenced the morphology and size of the self-cross-linked SiO_2, and biocoal with an open foam-like porous structure containing micro- and mesopores was obtained. Addition of KOH in the course of pyrolysis of mixtures of lignin and rice hulls with polyvinyl chloride favored an increase in the biocoal fraction by a factor of almost 2, to 52–55%.

Pyrolysis of binary mixtures in the presence of KOH led to the formation of a product with larger surface area compared to the biocoal prepared without activation by a factor of 15 in the case of lignin and by a factor of 4 in the case of rice hulls [65], which is associated with structural features of the carbon frameworks of the products. A study of the ability of the pyrolysis products to adsorb toluene showed that the product obtained from the lignin/PVC/KOH mixture had higher sorption capacity, 263.4 mg g^{-1}.

The biomass waste (paper, wood) and polyvinyl chloride, milled in a planetary mill, were subjected to joint pyrolysis at 600–800°C in an N_2 stream [66]. The hydrogen chloride released from polyvinyl chloride was partially sorbed in the course of joint pyrolysis in the pyrolysis semicoke to form functional C–Cl groups. The addition of a larger amount of polyvinyl chloride to the biomass (paper or wood) led to the formation of a solid residue with a smaller specific surface area, because molten polyvinyl chloride adhered to the paper and wood surface, blocking the development of the porous structure.

With an increase in the polyvinyl chloride content, the fraction of chlorine atoms in the semicoke increased. The temperature of 700°C and the biosubstrate to polyvinyl chloride ratio of 3 : 1 appeared to be the optimum pyrolysis conditions. The biocoal obtained by pyrolysis of the wood/polyvinyl chloride mixture had higher chlorine content.

Trials of the synthesized chlorinated biocoal as a sorbent of elemental mercury revealed its higher (by a factor of 2.5–5) performance in mercury removal compared to the untreated semicoke; the mercury removal efficiency reached 90% at 140°C. The mercury uptake by the chlorinated biocoal occurred as chemical adsorption, in contrast to simple physical adsorption on the surface of semicoke without chlorine.

The addition of $Fe(NO_3)_3$ to a mixture of biomass and polyvinyl chloride in one-step pyrolysis [66] led to the formation of magnetic Cl-biocoal with larger specific surface area [67], which showed higher performance, compared to the chlorinated biocoal obtained in [66], in mercury removal in a wider temperature range (25–220°C). The mechanism of the Hg^0 removal on the Fe/Cl-semicoke consisted in its chemisorption via binding with Fe_3O_4, C–Cl, and C=O active sites.

Joint pyrolysis of biomass and polyvinyl chloride wastes allows production not only of alternative fuel in the form of semicoke, but also of pyrolysis oils [59–64] surpassing in their quality the oils from pyrolysis of plastics waste. A sorbent for removing, e.g., toluene [65] and elemental mercury [66, 67] from wastewater can also be obtained. The addition of biomass to polyvinyl chloride in the course of pyrolysis decreased the temperatures of the onset and maximum of the polyvinyl chloride degradation and accelerated the biomass degradation owing to the HCl released from polyvinyl chloride, which acts as an acid catalyst. In this case, the fraction of pyrolysis oils slightly decreased and that of coke increased compared to the pyrolysis of the polyvinyl chloride waste. The formation of heavier aromatic compounds such as polycyclic aromatic hydrocarbons in joint pyrolysis of polyvinyl chloride and biomass was associated with the release of HCl, accompanying the internal cyclization and aromatization. Because degradation of biomass containing a large amount of oxygen atoms and of polyvinyl chloride in oxygen or air can lead to the formation of toxic chlorinated dioxins and dibenzofurans, the pyrolysis should be performed in an inert medium.

DECHLORINATION OF CHLORINE-CONTAINING PYROLYSIS OILS

Because the majority of pyrolysis oils obtained by thermal and catalytic degradation of plastics waste contain a large amount of chlorinated compounds, these compounds should be removed for the subsequent use of the oils either as a fuel or as a petrochemical feedstock.

The pyrolysis oils obtained by heat treatment (410°C) of municipal plastics waste consisting of polyethylene, polypropylene, polystyrene, polyvinyl chloride, and poly(ethylene terephthalate) were subjected to catalytic dechlorination over γ-Fe_2O_3, Fe_3O_4/C, ZnO, MgO, and RedMud [69] (Table 6).

γ-Fe_2O_3 showed the highest performance (95%, 30 ppm Cl), whereas MgO appeared to be the least active (78%, 132 ppm Cl), which may be associated with acid–base properties of the oxides. Iron oxide showed stability in the reaction for up to 5 h with constant maximal degree of dechlorination, whereas the dechlorination efficiency over MgO and ZnO after 5-h reaction was 20 and 30%, respectively, because of the formation of a salt “crust” ($MgCl_2$ [48] and $ZnCl_2$) on the catalyst surface, blocking the pores with acid–base sites. Even after 16-h use of γ-Fe_2O_3, the content of chlorinated organic compounds in pyrolysis oils did not exceed 30 ppm.

The pyrolysis oils obtained by degradation of plastics mixtures consisting of polyethylene (33%), polypropylene (33%), polystyrene (33%), and polyvinyl chloride (1%) were dechlorinated in the presence of iron oxide based catalysts, either unsupported (α-Fe_2O_3, γ-Fe_2O_3) or on a carbon support (Fe_3O_4/C) [70].

Ahmed et al. [71] suggested the mechanism of the polyvinyl chloride dechlorination over Fe_3O_4. Iron-containing catalysts in the course of dechlorination were deactivated owing to adsorption of gaseous hydrogen chloride formed in the reaction. Continuous adsorption of HCl on iron oxide converted it to $FeCl_2$. The adsorbed HCl can be continuously removed using a carrier gas such as He, thus prolonging the catalyst operation life and excluding its deactivation. The oil conversion over oxide catalysts was 95–99%, with Fe_3O_4/C showing the highest activity (99%) and stability; the fraction of chlorinated compounds in the spent oil did not exceed 50–70 ppm even after continuous operation of the catalyst for 25 h.

Lopez-Urionabarrenechea et al. [72] processed chlorinated heavy pyrolysis oils 1 and 2 obtained in [53] (Table 6), containing mainly styrene, toluene, and ethylbenzene, by thermal and catalytic cracking.

The degree of cracking in heat treatment of oils 1 and 2 was 87 and 67.5%, whereas in the catalytic process the conversion increased to 92.3 and 86.5%, respectively. With an increase in the degree of cracking, the relative content of the light and heavy fractions decreased and that of the gaseous products increased to 46.8 and 20.4% against 15.8 and 8.7% in heat treatment of oils 1 and 2, respectively. In all the cases, the major components of the light fraction were aliphatic hydrocarbons C_5–C_{10} (78–92%) and aromatic hydrocarbons C_{11}–C_{16}. The relative content of chlorinated compounds in heat treatment of oils 1 and 2 decreased to 0.2%, whereas in the catalytic process it decreased to less than 0.1%. Chlorinated branched aliphatic and aromatic compounds (C_6–C_{11}) in pyrolysis oils decomposed in the course of cracking with the release of gaseous HCl and thus transformed into dechlorinated condensable light fractions.

The heavy fractions (dark viscous products) also mainly consisted of C_5–C_{10} (up to 65.2% in pyrolysis oil 1 and up to 55.1% in pyrolysis oil 2); the fraction of C_{11}–C_{16} increased (to 28.8 and 30.3%, respectively), and hydrocarbons $>C_{16}$ appeared. The content of chlorinated

Table 6. Conditions of dechlorination of pyrolysis oils

Substrate	Chlorine content	Additive	Substrate/ additive	Conditions	Results	References
Pyrolysis oil obtained from municipal plastics waste (410°C)	600 ppm	γ-Fe_2O_3 Fe_3O_4/C ZnO MgO RedMud	–	350°C, He, 1–16 h	95% (1 h) 88% (1 h) 91% (1 h) 78% (1 h) 84% (1 h)	[69]
Pyrolysis oil from a mixture of PE (33%), PP (33%), PS (33%), and PVC (1%) (410°C)	1894 ppm	α-Fe_2O_3 γ-Fe_2O_3 Fe_3O_4/C	–	350°C, He	97% (1 h) 97% (1 h) 99% (1 h)	[70]
Pyrolysis oil from a mixture of PE (33%), PP (33%), PS (33%), and PVC (1%) (410°C)	0.8%	–	–	325°C, N_2	0.2% in LF* 0.1% in TF*	[72]
Pyrolysis oil from a mixture of PE (33%), PP (33%), PS (33%), and PVC (1%) (410°C)	0.8%	RedMud	100 g mixture/ 10 g catalyst	325°C, N_2	<0.1% in LF 4.5% in TF	[72]
Pyrolysis oil 2 from a mixture of PE (40%), PP (35%), PS (18%), PET (4%), and PVC (3%) (425–460°C, ZSM-5, 30 min)	0.9%	–	–	325°C, N_2	0.2% in LF 0.2% in TF	[72]
Pyrolysis oil 2 from a mixture of PE (40%), PP (35%), PS (18%), PET (4%), and PVC (3%) (425–460°C, ZSM-5, 30 min)	0.9%	RedMud	100 g mixture/10 g catalyst	325°C, N_2	<0.1% in LF 5.6% in TF	[72]

Note: PE, polyethylene; PP, polypropylene; PS, polystyrene; PVC, polyvinyl chloride; PET, poly(ethylene terephthalate); LF, light fraction; HF, heavy fraction.

organic compounds did not exceed 0.1 and 0.2% in heat treatment of pyrolysis oils 1 and 2 in a flow, and in the case of catalytic cracking it increased to 4.5 and 5.6%, respectively, which is due to the reaction of the major component of RedMud, Fe_2O_3, with the HCl released in the course of cracking to form $FeCl_3$.

The major fraction of chlorine released in the form of HCl was in the gas phase after the heat treatment of pyrolysis oils (80.6% in the case of oil 1 and 79.7% in the case of oil 2). When using RedMud, the percentage of the initial chlorine retained in the solid fraction increased to 43.3% in oil 1 and to 84% in oil 2; correspondingly, in the gas phase it decreased to 51% in oil 1 and to 8.7% in oil 2.

γ-Fe_2O_3 took up chlorinated compounds in pyrolysis oils from municipal plastics waste most efficiently, reducing the initial amount of chlorinated organic compounds to 30 ppm [69], whereas the Fe_3O_4/C composite proved to be the most active and stable (up to 25 h of continuous operation) among all iron-based sorbents [70]; in the course of recycling, it took up more than 1800 ppm Cl. As compared to the heat treatment of pyrolysis oils obtained by different procedures, the use of the RedMud sorbent led to the residual content of chlorinated organic compounds in spent oils lower than 0.1% [72].

MECHANOCHEMICAL DECHLORINATION

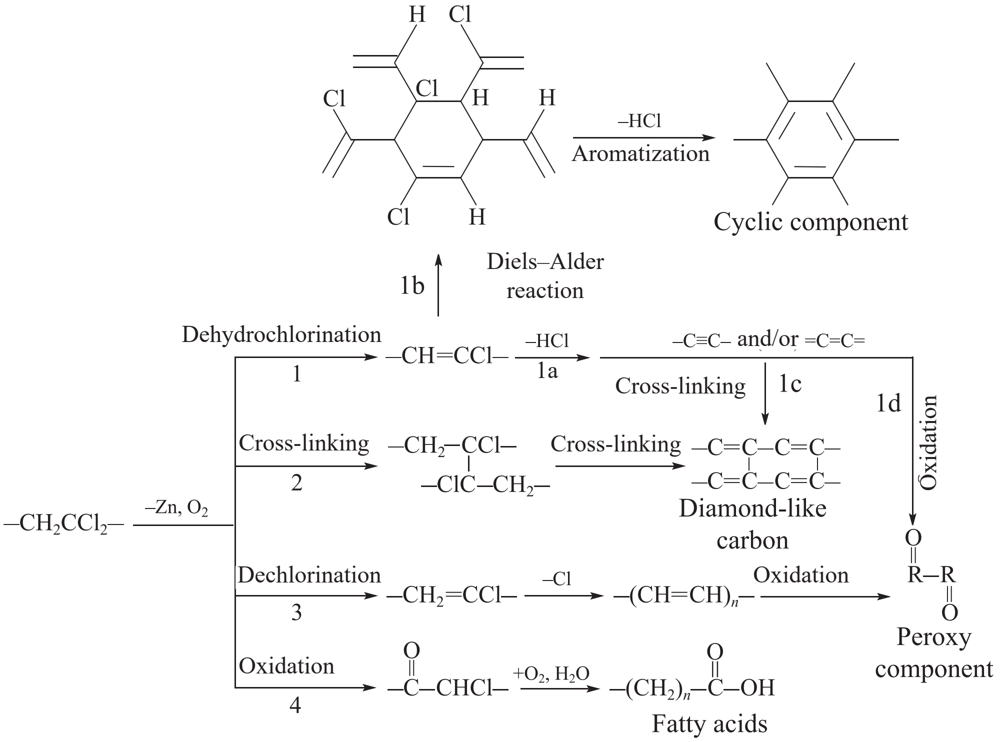
Mechanochemical dechlorination of chlorinated polymers is performed, as a rule, in a planetary ball mill using steel balls of different weight and size in different amounts at room temperature [73–81] and a filler required for binding hydrogen chloride. Metals [73], metal oxides [74–76], bases [77], and salts [79–81] are commonly used as fillers (Table 7).

Table 7. Conditions of polyvinyl chloride dehydrochlorination by the mechanochemical procedure

Polymer	Chlorine content, %	Additive	Me : Cl ratio	Conditions	Degree of dechlorination	References
PVC	35	Zn	(1–9) : 1, 30 g mixture	1–8 h, 24°C, O_2, milling	100%, (6–9) : 1, 3 h	[73]
PVDC	65	Zn	(1–9) : 1, 30 g mixture	1–8 h, 24°C, O_2, milling	100%, (4–9) : 1, 3 h	[73]
PVC	56.5	CaO	1 : 1, 3 g mixture	1–12 h, 24°C, O_2, milling	100%, 12 h	[74]
PVC	56.5	CaO, SiO_2	2 : 1, 3 g mixture	1–8 h, 24°C, O_2, milling	100%, 6 h	[75]
PVC	56.5	CaO	(1–4) : 1, 3 g mixture	1–6 h, 24°C, O_2, milling	92%, 4 : 1, 6 h	[76]
PVC	56.5	Fe_2O_3	(1–4) : 1, 3 g mixture	1–6 h, 24°C, O_2, milling	82%, 4 : 1, 6 h	[76]
PVC	56.5	SiO_2	(1–4) : 1, 3 g mixture	1–6 h, 24°C, O_2, milling	–	[76]
PVC	56.5	Al_2O_3	(1–4) : 1, 3 g mixture	1–6 h, 24°C, O_2, milling	–	[76]
PVC	52.8	NaOH	(1–4) : 1, 3 g mixture	3–12 h, 24°C, O_2, milling	97%, 4 : 1, 12 h	[77]
PVC	52.8	KOH	1-4 : 1, 3 g mixture	3–12 h, 24°C, O_2, milling	98%, 4 : 1, 12 h	[77]
PVC SS	22–24	NaOH (0.5–1 M)	100–200 g PVC	5 L EG[a], 1–5 h, 190°C	96% (30 rpm, 1.27 mm balls, 1 M NaOH/EG, 5 h)	[78]
PVC CC	28–32	NaOH (0.5–1 M)	100–200 g PVC	5 L EG, 1–5 h, 190°C	92% (45 rpm, 1.27 mm balls, 0.5 M NaOH/EG, 5 h)	[78]
PVC	56.7	$CaCO_3$ (mollusk shells)	(2–4) : 1, 3 g mixture	1–8 h, 24°C, O_2, milling	100%, 4 : 1, 4 h	[79]
PVC waste	47	$CaCO_3$ (eggshell)	5 : 1, 5 and 100 g mixture	1–12 h, 24°C, O_2, milling	100%, 4 h, 5 g mixture, 50%, 12 h, 100 g mixture	[80]
PVC	58	$LiCoO_2$ + NaOH, KOH, CaO, Fe_2O_3, SiO_2, Al_2O_3, Ni, Al or Fe	1 : 1	3–12 h, 24°C, O_2, milling	98.7%, +Fe (1/1/1), 12 h	[81]

[a] PVC, polyvinyl chloride; EG, ethylene glycol.

Scheme 4. Mechanism of mechanochemical dechlorination of polyvinylidene chloride with Zn.



The mechanical treatment of polymers or their mixtures with a filler involves generation of high internal stresses leading to scission of a macromolecular chain, i.e., to mechanochemical degradation. The C–C bond energy is negligibly low compared to the energy consumed even under very mild conditions of polymer recycling. Because the energy required for moving the macromolecules exceeds the chemical bond energy, the mechanical treatment leads to scission of separate molecular chains in the zone of occasional concentration of mechanical stresses.

Cleavage of a chemical bonds leads to generation of active fragments, free radicals R* and/or ions $R^{+/-}$, which subsequently participate in various chemical processes (isomerization, chain transfer, and chain termination). The detailed mechanism of such dechlorination involving not only the elimination of HCl (dehydrochlorination) and Cl (dechlorination), but also cross-linking and oxidation [73] is shown in Scheme 4 for polyvinylidene chloride as example.

Xiao et al. [73] studied the influence of the kind of the chlorinated polymer and of the size and weight of steel balls in the presence of Zn. Irrespective of the kind of the polymer, the degree of dechlorination increased with the reaction time (varied from 1 to 8 h) and molar ratio of Zn to Cl in the polyvinyl chloride/polyvinylidene chloride mixture (varied from 1 : 1 to 9 : 1). For example, 100% degree of dechlorination of polyvinylidene chloride was reached in 5 h at Zn/Cl = 4 : 1 and already in 1.5 h at Zn/Cl = 9 : 1.

Dechlorination of polyvinylidene chloride occurred considerably faster than that of polyvinyl chloride, which is associated with the structural difference between the polymers: The presence of two chlorine atoms bonded to the same carbon atom makes polyvinylidene chloride less stable to degradation, considerably facilitating the HCl removal from the polymer structure. The degree of dechlorination higher than 80% was reached in 2 h at all the Zn/Cl ratios for polyvinylidene chloride and only at the 9 : 1 ratio for polyvinyl chloride.

Diamond-like carbon formed by cross-linking of the chains (2) or carbyne fragments (1c) was the major product of dehydrochlorination of polyvinyl chloride and polyvinylidene chloride. The formation of cyclic compounds by the Diels–Alder reaction (1b) and of fatty acids occurred via oxidation. The dehydrochlorination, cross-linking of the carbyne fragment into polyacetylene, and its subsequent oxidation can lead to the formation of peroxy compounds. The reaction of Zn with HCl yielded zinc(II) oxychloride ($Zn_2OCl_2 \cdot 2H_2O$) and simonkolleite $Zn_5(OH)_8Cl_2 \cdot H_2O$.

The polyvinyl chloride dechlorination under the conditions of milling with CaO (CaO/Cl = 1 : 1) [74] was accompanied by the formation of the water-soluble chloride CaOHCl, which was removed using Na_3PO_4:

$$[CH_2CHCl]_n + CaO = CaOHCl + [CH{=}CH]_m$$

(n, m denote the degree of polymerization, $n > m$),

$$10CaOHCl(L) + 6\,Na_3PO_4(L) = Ca_{10}(PO_4)_6(OH)_2(S) + 10NaCl(L) + 8NaOH(L).$$

The solid carbonaceous residue obtained in the process (12 h) and filtered off did not contain even traces of chlorine, which allows its subsequent use as a fuel, and the hydroxyapatite formed can be used as a sorbent for wastewater treatment owing to its capability to sorb heavy metal cations.

An increase in the Ca/Cl ratio to 2 : 1 and the addition of SiO_2 to enhance milling of polyvinyl chloride in [75] considerably shortened the reaction time compared to [74]. In so doing, strong influence was exerted by the size of the planetary mill and, as a consequence, by the weight and amount of the steel balls used. For example, in a small planetary mill, the use of a larger admissible number of balls (7 balls) led to 100% degree of dechlorination already in 6 h. In a large planetary mill with the addition of small balls 4.8 mm in diameter (1560 balls), the maximal degree of dechlorination was 90% (8 h), and with an increase in the ball size (15.6 mm) and, correspondingly, with a decrease in their number (42 balls) the degree of removal of chlorine atoms in the same time was 88%.

The effect of oxides (CaO, Fe_2O_3, SiO_2, Al_2O_3) on the polyvinyl chloride dechlorination in air was studied in [76] (1–6 h). The dechlorination in the presence of these oxides occurred along two pathways: with the formation of chlorides CaOHCl [74] and $FeCl_2 \cdot 2H_2O$ when using CaO and Fe_2O_3 and with the release of gaseous HCl when performing the polyvinyl chloride degradation in the presence of SiO_2 and Al_2O_3, according to the X-ray diffraction patterns. In the process, SiO_2 and Al_2O_3 played an important role of grinding additives disintegrating polyvinyl chloride particles.

In contrast to CaO [74], which binds one chlorine atom in a structural unit of polyvinyl chloride, the iron atom from Fe_2O_3 interacts with two Cl atoms:

$$4\ –CH_2CHCl– + Fe_2O_3 \rightarrow 3\ –CH{=}CH– + –(CHCl–CHCl)– + FeCl_2 \cdot 2H_2O + FeO.$$

Therefore, the degree of dechlorination with Fe_2O_3 (40%) considerably exceeded that reached with CaO (18%) at the same molar ratio Me/Cl = 1 : 1 (6 h). Thus, the degree of dechlorination decreased in the order $Fe_2O_3 > Al_2O_3 > SiO_2 > CaO$. The degree of dechlorination increased not only with an increase in the milling time, but also with an increase in the amount of the oxide powder, i.e., in the Me/Cl molar ratio: 92% with Fe_2O_3 and 82% with CaO (Me/Cl = 4 : 1, 6 h).

The use of alkalis (KOH and NaOH) as fillers was studied in [77]. The peaks of metal chlorides appeared in the IR spectra already in 3 h.

In both systems (polyvinyl chloride/NaOH and polyvinyl chloride/KOH), the mean size of the mixture particles rapidly decreased in the initial step of milling, but then in the course of prolonged milling it gradually decreased owing to agglomeration of fine particles. The molecular mass of partially dechlorinated polyvinyl chloride in the polyvinyl chloride/KOH mixture was higher than in the polyvinyl chloride/NaOH mixture, because KOH mainly reacted with Cl atoms in polyvinyl chloride, whereas NaOH decomposed. The dechlorination rate of the polymer milled with KOH was higher than that of the polymer milled with NaOH because of slight difference in the electronic properties of potassium and sodium. The positive charge of K is larger than that of Na owing to larger radius and larger number of electronic shells; therefore, K^+ will react with Cl^- faster than Na^+ will. As in the previous studies, the degree of dechlorination increased with time and with the amount of the additive. At the ratio Cl : K/Na = 1 : 2, the reaction product in the polyvinyl chloride/KOH system (4 h) was a sticky orange paste, whereas that in the polyvinyl chloride/NaOH system was a yellow powder.

The polyvinyl chloride waste used in an industrial installation [78] consisted of refrigerator door gaskets (1) and electric cable (2) from recycling. For better milling of the polyvinyl chloride waste, it was initially treated with a NaOH for the surface dechlorination. This treatment led to the substitution of chlorine by –OH groups (S_{N2} reaction) and elimination of HCl to form C=C bonds (E2 reaction). Without ball grinding, the penetration of NaOH molecules into thick particles of polyvinyl chloride would be prevented by the formation double bonds on their surface due to E2 reaction; therefore, completely dechlorinated particles could not be obtained. The use of a higher NaOH concentration (>1 M) led to a stronger increase in the viscosity of the liquid, which negatively influenced the ball grinding and impaired oxidation with ethylene glycol oxygen atoms.

An increase in the rotation rate to 30 rpm and the addition of steel balls increased the degree of dechlorination of waste 1 in 1 M NaOH/ethylene glycol to 96%. The maximal degree of dechlorination of waste 2 (92%) was reached at 45 rpm in 0.5 M NaOH/ethylene glycol. The dechlorinated residue of both kinds of polyvinyl chloride waste (<100 μm) contained less than 1 wt % chlorine.

The use of biological wastes such as mollusk shells and eggshell, consisting of calcium carbonate, in polyvinyl chloride dechlorination was studied in [79, 80]. Milling of polyvinyl chloride waste and mollusk shells [79] led to disintegration of waste particles and to bond cleavage in them and thus favored the reaction with calcium carbonate to form calcium chloride already after 2-h milling with the formation of a polyene (data of IR spectroscopy).

$$[CH_2CHCl]_n + CaCO_3 = [CH{=}CH]_m + CaCl_2 + CO_2 + H_2O \text{ (}n, m\text{ is the degree of polymerization).}$$

More than 95% of chlorine was removed from polyvinyl chloride within 2 h of the reaction (Cl : Ca = 1 : 4, rotation at 700 rpm). As compared to the mixture of polyvinyl chloride with pure $CaCO_3$, no significant difference in the degree of dechlorination was observed, which demonstrates the efficiency of using mollusk shell waste as a sorbent for trapping the hydrogen chloride released from polyvinyl chloride.

In [80], the results of the laboratory experiments on recycling of polyvinyl chloride and eggshell wastes were applied to semicommercial trials [80], with increased reaction mixture weight and planetary mill volume. The use of higher Ca : Cl ratio compared to the previous studies [75, 76, 79] was dictated by the fact that the industrial polyvinyl chloride waste contained various additives and its chlorine content was lower than that of pure polyvinyl chloride. Kinetic analysis has shown that the dechlorination occurred 7 times faster at a higher Ca : Cl ratio (5 : 1) than at the Ca : Cl ratio of 2.3 : 1. The rate of the semicommercial process was 1.23×10^{-5} s^{-1}; i.e., it was approximately 5 times lower than in the laboratory experiments. For example, complete dechlorination in the laboratory experiment was reached in 4 h, whereas in the semicommercial process (100 g of the mixture) no more than 55% of chlorine was removed in 12 h.

Wang et al. [81] studied joint mechanochemical recycling of spent lithium-ion batteries containing cathode materials ($C/LiCoO_2$) and of polyvinyl chloride with various additives, followed by leaching with water. The Co and Li content of the cathode material was 51.8 and 6.5 wt %. In milling of $LiCoO_2$ and polyvinyl chloride without additives, the conversion of Li, Co, and Cl was 27.5, 1.4, and 13%, respectively.

In the presence of the added bases, the degree of dechlorination exceeded 60% and increased in the order NaOH < KOH < CaO ($LiCoO_2$/PVC/hydroxide weight ratio 1/1/1, 12 h). In the case of CaO, the degree of polyvinyl chloride dechlorination reached 90% owing to binding of calcium and chloride ions into calcium chloride, whereas the Li conversion decreased to 18%, which was caused by difficult binding of Li and Co due to the layered structure of $LiCoO_2$. The additions of the oxides Fe_2O_3, SiO_2, and Al_2O_3 also favored an increase in the degree of the polyvinyl chloride dechlorination to 87% (Al_2O_3); it increased in the order $Fe_2O_3 < SiO_2 < Al_2O_3$, like the Li conversion, which increased to 68% on adding Al_2O_3. These trends were due to better milling and, as a consequence, more efficient friction in the presence of aluminum oxide.

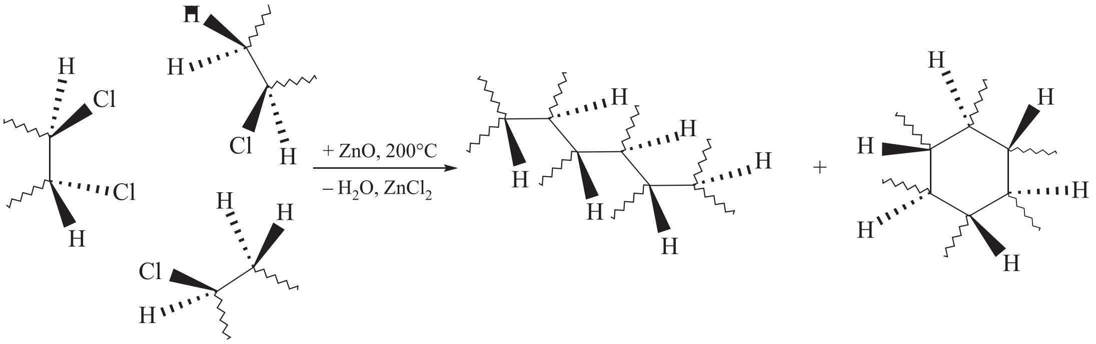
In polyvinyl chloride dechlorination in the presence of zerovalent metals (Ni, Al, Fe), the chlorine atom was bound to the metal atom (Ni, Al, or Fe) to form the chloride MCl_x, which, in turn, reacted with Li and Co to form $LiCoO_2$. Because of lower activity of Co compared to Li, LiCl and not $CoCl_2$ was formed. In the series Ni < Al < Fe, the degree of polyvinyl chloride dechlorination increased from 70.3 to 92.5%, and the lithium conversion, from 78.5 to 98.7%.

The best results were obtained on adding Fe; the restructurization yielded the magnetic material $CoFe_4O_6$. The optimum $LiCoO_2$/PVC/Fe ratio was 1/2/1, and the optimum reaction time was 12 h. The conversion of Li, Cl, and Co under these conditions was 100, 96.4, and 8.1%, respectively.

There are two types of mechanochemical recycling of polyvinyl chloride:

– in the presence of fillers acting as sorbents, such as metals, basic and amphoteric oxides, alkalis, and salts,

Scheme 5. Polyvinyl chloride dechlorination over ZnO (200°C).



binding the HCl released upon bond cleavage in the course of polyvinyl chloride milling with a decrease in its molecular mass;

– in the presence of fillers acting as grinding agents, such as SiO_2 and Al_2O_3 [76].

Many authors reached 100% efficiency of the polyvinyl chloride dechlorination by increasing the molar ratio of the active metal to chlorine (in terms of the $–CH_2–CHCl–$ groups in polyvinyl chloride) [73] or by increasing the process time to 12 h [74]. At the maximal reaction time (12 h) under similar conditions, CaO showed higher performance [75] compared to NaOH and KOH [77]. The addition of SiO_2 as a grinding agent in milling of the CaO/polyvinyl chloride mixture decreased the process time without efficiency loss [75].

The dechlorination of polyvinyl chloride waste (100–200 g) by primary dechlorination with solutions of alkalis in ethylene glycol [78], followed by grinding with NaOH, ensured less than 1 wt % chlorine content of the dechlorinated polyvinyl chloride residues (<100 μm).

The results of experiments with laboratory sorbents and pure polyvinyl chloride allowed scaling of the process [73] and dechlorination of polyvinyl chloride waste in the presence of biological [79, 80] and technical wastes [81].

One of the drawbacks of this procedure for polyvinyl chloride waste processing is the need for washing of the residue to remove metal chlorides formed in the process, followed by the wastewater treatment. The main advantages of the mechanochemical dechlorination of polyvinyl chloride consist in performing the grinding at room temperature in air, which considerably reduces the power demand, makes the use of inert carrier gases unnecessary, and eliminates corrosion of the metal equipment compared to pyrolysis; it ensures the formation of chlorine-free dechlorinated residues.

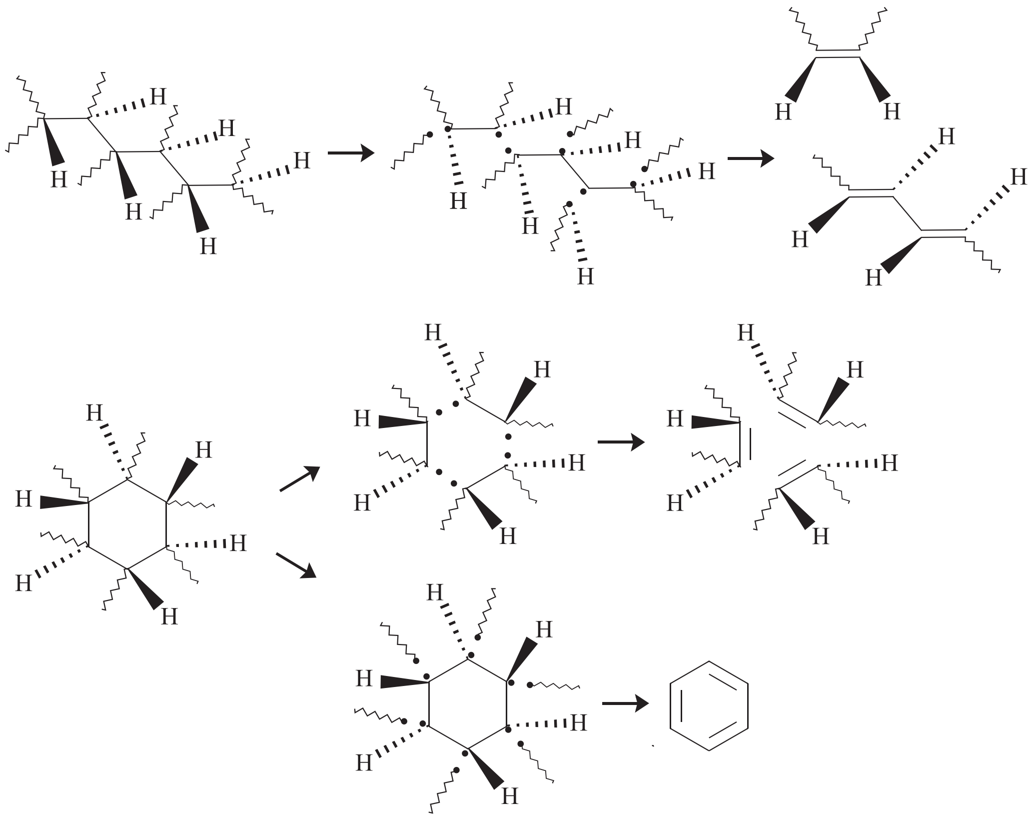
LOW-TEMPERATURE CATALYTIC DECHLORINATION

As a rule, the weight loss of pure polyvinyl chloride on heating in a nitrogen stream starts at approximately 250°C and occurs in the interval 250–350°C [82]. On adding calcium oxide, the weight loss was observed in the same temperature range with the only difference that the weight loss was smaller because of the formation of nonvolatile $CaCl_2$ instead of HCl. The use of ZnO as an HCl sorbent decreases the weight loss onset temperature to 200°C. The main reaction in the presence of ZnO is cross-linking of a C–C single bond in a polymer chain or between polymer chains, followed by the conversion to aliphatic $(CH)_n$ polymer or to aromatic compounds via molecular cyclization or chain scission (Scheme 5).

Based on the data of transmission electron microscopy and IR spectroscopy, the authors assumed that the solid-phase reaction occurred at 200°C via formation of the liquid phase of zinc chloride, which acted as the reaction promoter. The second step was isomerization of aliphatic $(CH)_n$ polyene into benzene-type aromatic compounds (Scheme 6). Because the cross-linking occurs at a lower temperature (200°C) than the temperature at which the isomerization becomes possible, aromatic products are not formed.

The major fraction (up to 73%) of the hydrogen chloride released in the course of the polyvinyl chloride degradation reacted with ZnO (5 h) with the release of water and formation of soluble zinc salts [$Zn_2OCl_2·2H_2O$, $Zn_5(OH)_8Cl_2·H_2O$]; a small amount of HCl (~0.4%) remained (Table 8). As in mechanochemical

Scheme 6. Polymerization of aliphatic $(CH)_n$ polyene.



dechlorination [73–81], no chlorinated organic compounds were detected.

Performing the polymer dehydrochlorination in the presence of ZnO at a lower temperature (150°C) in [83] was dictated by the presence of polyvinylidene chloride, whose degradation temperature is 120°C, in the mixture with polyvinyl chloride; the HCl elimination started already at 190°C. In addition, the choice of the low process

Table 8. Conditions of polyvinyl chloride dechlorination in the presence of fillers

Polymer/copolymer	Chlorine content, %	Additive	Substrate/ additive ratio	Conditions	Degree of dechlorination	References
PVC	35	ZnO	1 : (0.75–0.3)	190–300°C, 30 min, 5 h, N_2	73%, 200°C, 5 h, ZnO/monomer = 3/1	[82]
PVC (35%)–PVDC (65%) copolymer	67.45	ZnO	1 : 1.6	150–170°C, N_2, 30 min	22%	[83]
PVC (35%)–PVDC (65%) copolymer	67.45	ZnO	1 : 1.6	THF, 150–170°C, N_2, 30 min	92%	[83]
PVC (70%), PVDC (20%) and CPE (10%)	42.3 in mixture	–	–	220–300°C, 800 W	65%, 75% HCl gas	[18]
PVC (70%), PVDC (20%) and CPE (10%)	42.3 in mixture	SiC	1 : 2	280°C, 800 W	84%, 83% HCl gas	[18]
PVC (70%), PVDC (20%) and CPE (10%)	42.3 in mixture	Graphite	1 : 2	280°C, 800 W	81%, 82% HCl gas	[18]

Note: PVC, polyvinyl chloride; PVDC, polyvinylidene chloride; CPE, chlorinated polyethylene; THF, tetrahydrofuran.

temperature is governed by the use of tetrahydrofuran as a solvent in dechlorination of chlorinated polymers [84]. The mechanism of the dehydrochlorination of this copolymer was similar to the mechanism described in [82]; the heat treatment of the reaction products led to the formation of microporous carbonaceous compounds with the specific surface area of 500–529 $m^2 g^{-1}$.

When performing the reaction in tetrahydrofuran, the degree of dechlorination at the given temperature (150°C) considerably increased (92%, 30 min) compared to the solid-phase dechlorination (22%, 30 min). The efficiency of the dechlorination in the solvent was caused by an increase in the area of contact of ZnO with PVC/PVDC due to the diffusion of $ZnCl_2$ formed in the acid solution into the copolymer matrix.

Liu et al. [18] studied the effect of the microwave radiation (800 W) on the PVC/PVDC/CPE waste mixture, where CPE is chlorinated polyethylene [18]. Variation of the dechlorination temperature in the interval 220–300°C showed that 280°C was the optimum temperature ensuring the highest degree of dechlorination (60%) with the formation of the larger amount of gaseous hydrogen chloride. The addition of graphite and silicon carbide (SiC) increased the degree of dechlorination and the amount of gaseous HCl by 20–25%. Experiments at varied heating rate (4–15 deg min^{-1}) showed that the optimum combination of high degree of dechlorination and large amount of gaseous HCl was reached at a heating rate of 9 deg min^{-1}: At 4 deg min^{-1}, the degree of dechlorination was maximal, but the relative amount of gaseous HCl did not exceed 50%, whereas at the maximal heating rate both parameters decreased because of the shorter process time. Thus, the content of Cl atoms in the solid reclaimed fuel was as low as 0.328%, and with respect to the calorific value (20.6 MJ kg^{-1}) the product was comparable to brown coal and bitumen coal.

Like mechanochemical recycling of polyvinyl chloride, low-temperature dechlorination does not lead to the formation of liquid chlorinated organic compounds, which it its main advantage. Dechlorination of such type occurs owing to the formation of a liquid promoter, e.g., $ZnCl_2$ [82, 83], with the formation of water and zinc chlorides soluble in it. Performing the reaction with the sorbent in a liquid medium using tetrahydrofuran considerably improved the quality of the dechlorinated product; the degree of dechlorination was 92% [83].

The effect of microwave radiation on the polymer degradation recently became a topical line of research in the field of dechlorination of chlorine-containing waste. The use of microwave radiation in dechlorination of a PVC/PVDC/CPE mixture in the presence of an adsorbent allowed removal of up to 84% of chlorine atoms from the chlorinated polymer mixture [18]; the calorific value of the semicoke obtained was similar to that of brown coal and bitumen, and the chlorine content was as low as 0.328%.

COPOLYMERIZATION/THERMAL OXIDATION

Thermal oxidative degradation of polyvinyl chloride in dioctyl phthalate at 200°C was studied in [85] (O_2, 1–6 h). The addition of this plasticizer considerably accelerated the polyvinyl chloride degradation with the release of free HCl relative to pure polyvinyl chloride; the process occurred already at 200°C. Accelerated dechlorination was accompanied by rapid chain scission without noticeable cross-linking. The degradation product (30 min–3 h) was a white to yellow solid substance. At a longer reaction time (4–6 h), the solid product transformed into brown oil. This fact suggested the occurrence of the oxidative cleavage of polyenes, leading to a decrease in the molecular mass of the fragments. The chain scission mainly occurred in the center of the conjugated polyene chain.

At longer degradation times, polyenes of lower molecular masses were obtained. Already after oxidative degradation for 3 h, the molecular masses of the majority of the degraded chains were lower than 1000 g mol^{-1}. The presence of carbonyl (1725 cm^{-1}) and hydroxyl (3460 cm^{-1}) absorption bands in the IR spectra proved the formation of the partially oxidized polyvinyl chloride.

The results obtained show that the presence of phthalate plasticizers will considerably accelerate the polyvinyl chloride degradation, which will favorably influence the degree of dechlorination in pyrolysis of flexible polyvinyl chloride and municipal plastics waste containing polymers of this type.

CONCLUSIONS

The results of studies on mechanochemical and thermal recycling of polyvinyl chloride, including low-temperature dechlorination and pyrolysis both of pure polyvinyl chloride and of its mixtures with other polymers and biomass, are summarized in this review. Analysis of published data allows the following conclusions.

– In the case of low-temperature recycling, the mechanism of the polyvinyl chloride degradation consists in the evolution of hydrogen chloride and formation of polyene, and in the case of pyrolysis it consists in the polymer degradation followed by cracking of the compounds formed.

– The use of metal oxide catalysts as sorbents for the HCl released in the course of catalytic degradation and dechlorination allows the fraction of gaseous chlorine and chlorine in liquid products to be considerably decreased. The ability to take up chlorine depends on the oxide basicity, and the catalytic performance, on its acid function.

– In pyrolysis of the binary mixture of polyvinyl chloride with other polymers, the addition of polystyrene, polystyrene/polyethylene mixture, acrylonitrile–butadiene–ethylene–styrene copolymer, and poly(ethylene terephthalate) favors the polyvinyl chloride degradation at lower temperatures, whereas the presence of polyethylene, on the contrary, increases the degradation temperature. The addition of all the polymers to polyvinyl chloride in a binary mixture increases the yield of liquid products and considerably decreases their chlorine content. Thus, joint recycling of polyvinyl chloride and other polymers should be performed only with monitoring of the feedstock composition.

– Addition of poly(ethylene terephthalate) to multicomponent mixtures containing polyvinyl chloride decreases the content of chlorine atoms in gaseous and liquid products, whereas on adding it to mixtures containing chlorinated and brominated wastes the fraction of chlorine, on the contrary, increases and the fraction of bromine decreases.

– Joint pyrolysis of polyvinyl chloride with biomass is extremely promising. In this case, the biomass degradation temperature considerably decreases and the dehydrochlorination accelerates, which is associated with the catalytic properties of the HCl released from polyvinyl chloride in cellulose dehydration and degradation.

– By analogy with mechanochemical recycling of pure polyvinyl chloride using various inorganic sorbents such as metals and metal oxides, hydroxides, and salts, it is appropriate to use as fillers biological (oyster shells, eggshell) and technical wastes (lithium–ion batteries) in dechlorination of polyvinyl chloride waste, which opens prospects for joint recycling of different kinds of wastes.

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CONFLICT OF INTEREST

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