

# Accepted Manuscript

Environmentally-friendly organochlorine waste processing and recycling

Sergei A. Kurta, Alex A. Volinsky, Mykola S. Kurta

PII: S0959-6526(13)00317-X

DOI: [10.1016/j.jclepro.2013.05.010](https://doi.org/10.1016/j.jclepro.2013.05.010)

Reference: JCLP 3447

To appear in: *Journal of Cleaner Production*

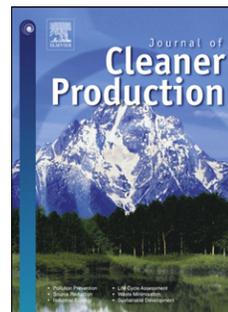
Received Date: 20 November 2012

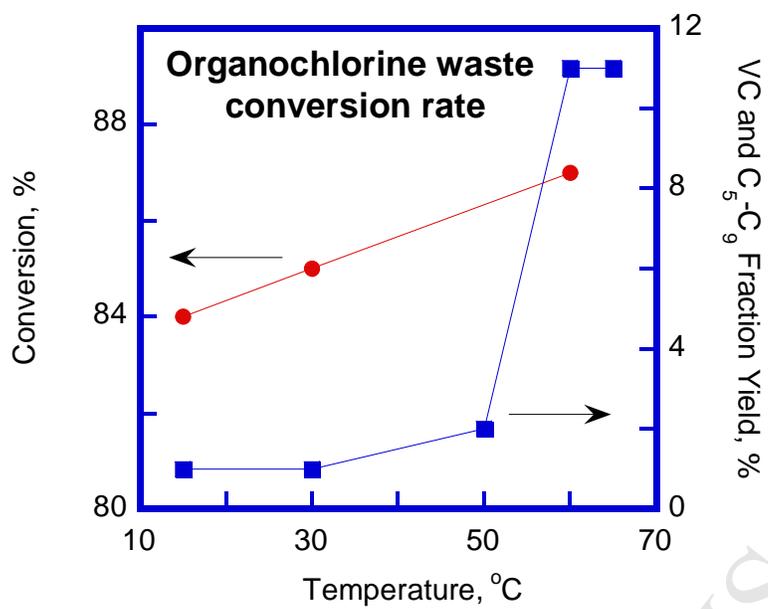
Revised Date: 12 May 2013

Accepted Date: 12 May 2013

Please cite this article as: Kurta SA, Volinsky AA, Kurta MS, Environmentally-friendly organochlorine waste processing and recycling, *Journal of Cleaner Production* (2013), doi: 10.1016/j.jclepro.2013.05.010.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.





- Compound processing of organochlorine wastes into products is presented:
- Repeated chlorination and alkaline dehydrochlorination
- Copolymerization with unsaturated C<sub>5</sub>-C<sub>9</sub> fraction
- Polycondensation with sulfide-containing wastes
- As a result, the amount of byproducts, currently burned, is reduced by 80-90%

ACCEPTED MANUSCRIPT

**Environmentally-friendly organochlorine waste processing and recycling**Sergei A. Kurta <sup>1</sup>, Alex A. Volinsky <sup>2</sup>, Mykola S. Kurta <sup>2</sup>

<sup>1</sup> Vasyl Stefanyk Precarpathian National University, Institute of Natural Science, Department of Organic and Analytical Chemistry, 57 Shevchenko Str., 76025 Ivano-Frankivsk, Ukraine. E-mail: kca2007@mail.ru

<sup>2</sup> Department of Mechanical Engineering, University of South Florida, 4202 E. Fowler Ave., ENB118, Tampa FL 33620, USA

**Abstract**

Due to environmental concerns, there is a need to enhance conversion to product and to prevent generation of wasteful byproducts and loss of organochlorine compounds in chemical production processes. The paper focuses on making vinyl chloride monomer production more efficient, and on possible ways of industrial organochlorine waste recycling. Environmentally-friendly processing and recycling methods of organochlorine waste are considered. Typical waste products are 1,2-dichloroethane, 1,1,2-trichloroethane, vinylidene chloride, and vinyl chloride monomer. Polymerization and copolymerization of typical waste with and without the C<sub>5</sub>-C<sub>9</sub> fraction resulted in non-toxic polymer products that can be used in the construction industry. The possibility of joint chlorine and sulfide-containing chemical waste recycling into polysulfide oligomeric products (Thiokol) is discussed. This comprehensive recycling allows utilizing 80-90% of all waste, generated during synthesis of chlorinated products. The results of this study aim to improve vinyl chloride monomer yield and minimize the formation of organochlorine waste by processing and recycling of byproducts into useful

products, including vinyl chloride monomers, vinylidene chloride, and other oligomers and polymers.

**Keywords:** organochlorine waste; byproduct; recycling; dichloroethane; vinyl chloride; trichloroethane.

## 1. Introduction

Vinyl chloride monomer (VCM) is one of the most used chemicals in the world. During the earliest attempts of vinyl chloride production, the reaction of acetylene and hydrogen chloride in the presence of mercuric chloride catalyst was carried out (Conte et al., 2007). Now, vinyl chloride commercial production involves pyrolytic decomposition of ethylene dichloride (EDC, also known as 1,2-dichloroethane). EDC can be produced by catalytic oxychlorination of ethylene in the presence of hydrogen chloride and oxygen, or by direct chlorination of ethylene. EDC pyrolysis produces vinyl chloride (VC), along with the same amount of hydrogen chloride as a co-product, one of the reactants in ethylene oxychlorination (Al-Hajri et al., 2010). Thus, having been produced in the pyrolytic reactor, hydrogen chloride is recycled in the oxychlorination reactor. Balanced VCM production process from ethylene and chlorine, without net consumption or hydrogen chloride generation, was developed by combining direct chlorination, EDC pyrolysis, and oxychlorination processes (Al-Hajri et al., 2010).

Typical VCM production plant includes six technological stages: 1) direct chlorination of ethylene; 2) oxychlorination; 3) purification of EDC; 4) thermal cracking of EDC; 5) purification of VCM; 6) burning organochlorine waste (OCW) (Lakshmanan et al., 1999). In addition to the main products, various byproducts accompany EDC/VC

production stages. Most significant byproducts in the oxychlorination reactor are 1,1,2-trichloroethane, chloral (trichloroacetaldehyde), cis- and trans-1,2-dichloroethylenes, mono-, di-, tri-, tetrachloromethanes, and carbon oxides. In the direct chlorination network, 1,1,2-trichloroethane is also produced. Acetylene, ethylene, butadiene, methyl chloride, chloroprene, vinylidene chloride, benzene, trichloroethylene, tri- and tetrachloromethane, and other various chlorinated products are produced in the pyrolysis reactor (Lakshmanan et al., 1999). Many of such byproducts are hazardous and toxic (Ding et al., 2013). Moreover, handling and disposal of those products are expensive. Furthermore, the amount of byproducts should be minimized to improve conversion of raw materials to desired products, lower raw materials cost, simplify EDC purification, prevent coking and fouling of the pyrolysis reactor, and reduce waste handling and treatment costs. The feed to the pyrolysis reactor should be at least 99.5% of pure dry EDC. In addition, EDC, recovered from the pyrolysis reactor, contains an appreciable amount of impurities. Some of these impurities, for example chloroprene, polymerizes to a rubbery material, which can seriously foul the EDC purification section (McPherson et al., 1979). Similarly, trichloroethylene can form an azeotrope with EDC. If this byproduct is not removed during EDC recycling from the pyrolysis stage, it can lead to the reduced cracking rates and increased reactor fouling (McPherson et al., 1979). Hence, there is a significant need to improve the performance of these reactors.

The disposal of OCW by incineration has been the subject of a large number of studies. Noteworthy, thermal treatment techniques are regulated by law (Thornton, 2002). Thermal treatment of OCW produces large quantities of hydrochloric acid (Ding et al., 2013). However, the level of exhaust gases should not exceed certain levels of

hydrochloric acid, chlorine, and dioxin equivalents (Innovation Technology Environment Quality requirement). According to the United Nations agreement, the level of dioxin equivalents has to be less than  $0.1 \text{ ng/m}^3$  (The United Nations Environment Programme. International Environmental Governance: Multilateral Environmental Agreements, 2001). The decomposition must be complete, and the chlorinated fractions have to be transformed into hydrochloric acid, carbon dioxide, and water, requiring extremely high temperature or expensive catalyst. Therefore, the treatment of exhaust gases according to these conditions, involves new stages, which are costly (Papp, 1996).

The method we propose is adjusted to the existing production of VC and will not require expensive changes. The annual VC production at “Carpathian-Petrochemical Ltd.”, a part of “Lukoil Group” in Kalush, Ukraine, constitutes 350,000 t/y (Kurta, 2012). The world production is about 32 Mt/y (Thornton, 2002). Currently all production waste is burned, producing OCW-containing hydrochloric acid (HCl) (Kurta 2011, Borruso, 2006). This OCW disposal results in 1.5 M US dollars losses per year. Approximate chemical composition of organochlorine waste from EDC and VC production, determined by chromatography, is shown in Table 1. OCW also contains a small amount of dissolved hydrogen chloride and chlorine. Amount of water in OCW does not exceed 20-200 ppm.

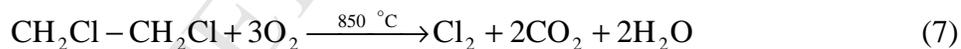
These reactions describe perchlorinethylene (tetrachloroethylene) incineration processes, which result in OCW during VC and EDC production:

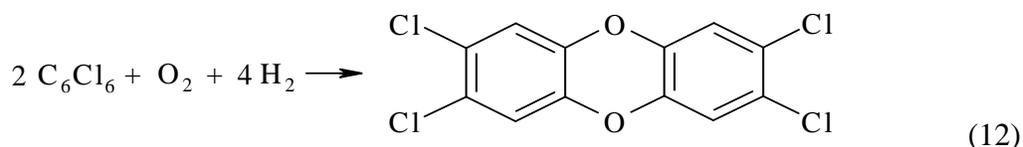




Reaction 4 shows the merge of aggressive chlorine and water. It requires the temperature of more than 1000 °C and  $\Delta H=57.5$  kJ/mol in order to complete the reaction (Hazel, 1989).

During OCW incineration, with EDC as an example, multiple satellite reactions occur that produce free chlorine, phosgene (Papp, 1996), and polychlorinated dibenzo-p-dioxins (Hung et al., 1989). Full combustion of 1,2-Dichloroethane follows:





### 1.1 Reduction of byproducts

The amount of OCW in the industry can be reduced, but cannot be avoided completely. Moreover, considering the industrial production scale, even as little as 3% of byproducts yield an enormous amount of waste. For example, the total amount of chemical waste, produced in various processes and involved in EDC/VCM synthesis, is estimated between 3% and 10% of the VCM yield, staggering 0.57 Mt to 1.9 Mt of byproducts each year (Thornton, 2002). Increasing production of chlorine-containing monomers and polymers is accompanied by larger amounts of industrial OCW (Allen et al., 1971). The most significant amounts of chlorinated waste are generated at the EDC, VC-monomer, and other organic chlorine compounds production stages (Naworski et al., 1983). Due to the increasing prices on hydrocarbons (natural gas and oil) and environmental degradation, it is important to investigate alternative cost-effective and environmentally-friendly methods of feedstock production (Lamberti et al., 2001), recycling and disposal of OCW, rather than their simple burning (Kurta, 2011). Thus, it was decided to further improve technological methods of processing and disposal of EDC and VC by complex processing of OCW into useful commercial products: VC monomers, vinylidene chloride (VDC), oligomeric, and polymeric products. This method preserves the hydrocarbons and chlorine, as well as ensures a higher level of environmental safety and economic benefits (Kurta et al., 2006).

## 2. Materials and methods

### 2.1 Industrial chlorine organic waste

Chemical composition of OCW from “Carpathian-Petrochemical Ltd.” production, determined by chromatography, is shown in Table 1. OCW contains insignificant amounts (ppm) of dissolved chlorine, hydrochloric acid, and not more than 20-200 ppm of water. The process of OCW burning is not economical, because all chlorine in synthesis products, including 1,2-EDC and 1,2,3-trichloroethane, which account for 50-70% of all OCW, is destroyed (Borruso, 2006). Thus, the thermal treatment of such waste produces a large quantity of hydrochloric acid.

It is not possible to obtain pure, concentrated hydrochloric acid because of OCW contamination by other byproducts (Papp, 1996). OCW burning leads to the complete loss of bound chlorine, when acid is neutralized by the alkaline. OCW burning leads to gaseous phosgene and chlorine, while even incomplete dioxins burning, in turn, leads to environmental pollution (The United Nations Environment Programme. International Environmental Governance: Multilateral Environmental Agreements, 2001). The amount of energy spent on OCW synthesis and disposal is huge. In particular, while burning 7,000 t of OCW, including 2,000 t of ethylene and 3,000 t of chlorine, 1,746,000 m<sup>3</sup> of natural gas are spent, and 300,000 m<sup>3</sup> of hydrogen are wasted, along with electricity, steam, other resources and materials (Kurta, 2012). As a result, 4,200 t of hydrochloric acid forms, requiring 4,600 t of alkaline solution to neutralize it. It is possible to minimize OCW utilization losses by shifting to lower OCW catalytic oxidation temperature (Manning, 1984).

## 2.2 Sulfide-containing alkalines

The sulfide-containing alkaline solutions are waste from olefins production. They are formed from ethylene-propylene production during alkaline washing of the pyrolysis products from H<sub>2</sub>S and CO<sub>2</sub> acid gases. The alkaline sulfide solutions contain 12-20wt.% sodium sulfide and 4-6wt.% sodium hydroxide. Currently there are no effective ways to recycle sulfide-containing alkaline. The plant with 250,000 t/y ethylene and propylene production capacity forms nearly 7,000 t/y of sulfide-containing alkaline waste (Kurta, 2012).

## 2.3 C<sub>5</sub>-C<sub>9</sub> monomers fraction

The C<sub>5</sub>-C<sub>9</sub> fraction is a volatile transparent liquid with a weak oily odor, insoluble in water. It is formed as a side product from the diesel fuel pyrolysis (Manning, 1984). The main physical properties of this fraction are listed in Table 2. The C<sub>5</sub>-C<sub>9</sub> fraction is a flammable and toxic class 2 product. It is carcinogenic, causes acute inflammation and chronic skin eczema, and has a strong narcotic effect (Papp, 1996).

## 2.4 Characterization methods

The description of experimental equipment setup for alkaline dehydrochlorination of OCW is presented in Figure 1. The alkaline dehydrochlorination of OCW experiment was conducted in the laboratory setting. To the 1 L reaction vessel (Claisen flask), previously purged with nitrogen, and equipped with the mixer, thermometer and condenser, 350 g of 30wt.% NaOH aqueous solution and 30 g of lime slurry (30wt.%

solution of calcium chloride in water) were added. The final ratio of NaOH and Ca(OH)<sub>2</sub> was 1:(1.5-2). The reaction mixture (OCW and alkalines) was stirred at 50-750 °C for 1-2 hours (150-300 rpm). The conversion rate of both dichloroethane and trichloroethane was 95-96%. Vinyl chloride was obtained with 95% yield from dichloroethane, while vinylidenechloride was obtained with the same yield from trichloroethane. OCW polymerization and co-polymerization with the C<sub>5</sub>-C<sub>9</sub> fraction, and OCW polycondensation with sulfide-containing alkalines were carried out in the custom-built laboratory reactor autoclave. This reactor was made from stainless steel with the volume of one liter, as shown schematically in Figure 2. Products of alkaline dehydrochlorination of OCW (vinyl chloride and vinylidene) were added to the reactor, equipped with the mixer, thermometer, and a heating jacket, followed by the C<sub>5</sub>-C<sub>9</sub> fraction addition with AlCl<sub>3</sub>. The reaction mixture was stirred for 4 hours at 900 °C and monitored by gas-liquid chromatography.

OCW was analyzed by gas-liquid chromatography. The analysis was carried out using Carlo Erba GC 8000 series chromatograph with a flame ionization detector. The following conditions were used for the analysis: 3 m working column length with 3 mm diameter; sorbent - 12% polyethylene glycol-1500 on chromium-oxide with the silica gel; 100-150 °C working temperature of the column; 190 °C evaporator temperature; 50 min analysis time; helium was used as the carrier gas. For the chromatogram calculations, the internal evaluation method was used (Beesley et al., 2001).

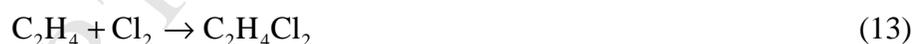
When studying chlorination of the unsaturated OCW, calculation of the required chlorine amount was conducted stoichiometrically, based on the content of chloroprene in

low-boiling OCW after its condensation. Iron shavings were used as a catalyst to intensify the chlorination of chloroprene, in the 1-10wt.% amount of the low-boiling OCW. The chlorination experimental conditions were as follows: 1) 100 ml volume of liquid OCW; 2) 25 °C temperature of the initial mixture; 3) 8.7wt.% chloroprene content in the initial OCW mixture; 4) 5-60 min time of feeding chlorine; 5) 52-625 ml/min chlorine flow rate; 6) reaction mixture temperature during chlorination increased by about 50 °C from the initial temperature.

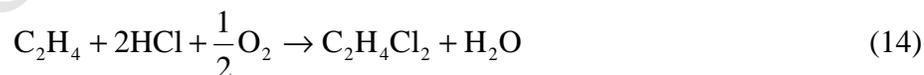
Based on the chromatography data, the products with the boiling temperature higher than 1,2-dichloroethane were obtained during chlorination. Their composition and chlorination reactions are described in the next section.

### 3. Results and discussion

VC and EDC are produced by straight catalytic chlorination of ethylene (Cowfer and Magistro, 1983). 1,2-EDC is produced by direct ethylene chlorination:



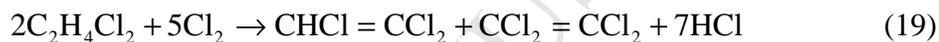
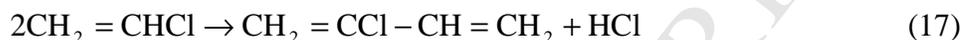
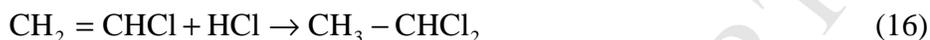
Catalytic oxychlorination of ethylene follows the reaction:



Vinyl chloride is produced by EDC pyrolysis at 520 °C:



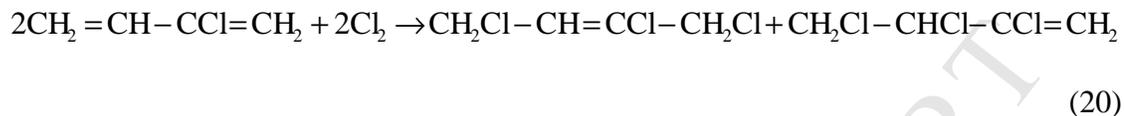
Besides the main products, there are other byproducts, including ethyl chloride (reaction 16), butadiene chloride (reaction 17), 1,1,2-trichloroethane (reaction 18), trichloroethylene, and tetrachloroethylene (reaction 19):



Other OCW components are presented in Table 1. Currently all this liquid and gaseous OCW is being incinerated, while generated solid waste requires more expensive treatment before utilization (McPherson et al., 1979).

During the first stage of this study, recycling of the primary OCW from vinyl chloride production was conducted by exhaustive chlorination, which may also decrease the amount of dioxins in OCW (Kurta, 2012). The presence of unsaturated hydrocarbons in OCW prevents these hydrocarbons from being used as hydrocarbon raw materials for making chloride-based products (Mitoma et al., 2001). It also complicates EDC and VC production processes due to polycondensation and polymerization in rectification columns. It has been shown that one of the ways converting unsaturated compounds into saturated is chlorination. (Zakrzhevsky and Kurta, 2006). Thus, higher EDC and VC yields can be achieved, along with less contamination of distillation columns (Kurta, 2012).

The chlorination reaction of unsaturated hydrocarbons contained in OCW is described below:



Chloroprene undergoes 1,4-addition reaction with the formation of 1,2,4-trichlor-2-buten and 2,3,4-trichlor-1-buten (20)

1,1,2-trichlorethane is obtained from chlorination of VC:



EDC reacts with chlorine and forms 1,1,2-trichlorethane:



The substitution reaction between benzene and chlorine results in the chlorobenzene and hexachlorobenzene formation:



Concentration of saturated OCW (chloroprene, 1,1-DCE, ethyl chloride) reduces almost to a minimum during chlorination (Figure 3). Based on these results, it is possible to utilize unsaturated OCW by chlorination before the rectification stage to obtain additional 15% of EDC (see Figure 4). At the same time, the amount of unsaturated compounds

decreases from 12% to 1% (Figure 3). Chlorine has no significant effect on the composition of saturated OCW, but joint processing with unsaturated OCW mixture is also recommended (Bae et al., 2001). Chlorination of light-boiling OCW from the main EDC and VC production rectification columns is suggested, based on this study. 1,2-EDC and 1,1,2-trichloroethane can be returned to the production process, reducing the amount of unsaturated OCW. Unsaturated OCW chlorination increases 1,2-dichloroethane content by 9-15%, and reduces 1,2-dichloroethane losses when burned.

The second part of this work considers EDC processing into VC, and trichloroethane processing into vinylidene chloride. Based on EDC and 1,1,2-trichloroethane, the following reactions occur during alkaline dehydrochlorination of OCW:

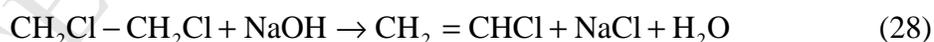
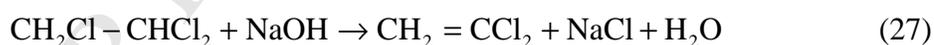
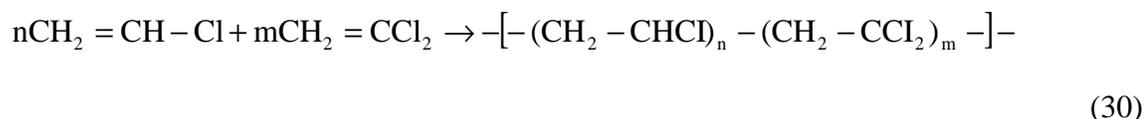


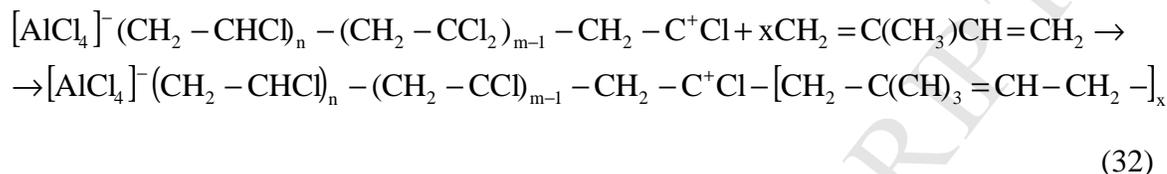
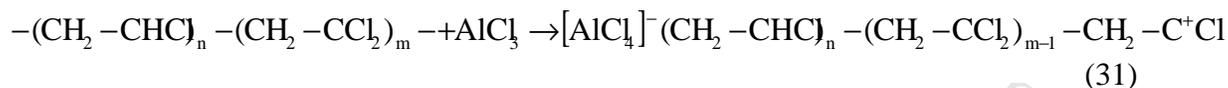
Figure 4 shows VDC and VC yield dependence on NaOH concentration in the dehydrochlorinated OCW mixture (Kurta et al., 2007). Based in Figure 5, the method of alkaline dehydrochlorination of OCW can also be recommended for OCW treatment and disposal, namely 1,2-EDC conversion into VC, and 1,1,2-trichloroethane into VDC.

Freshly prepared  $\text{Ca}(\text{OH})_2$  suspension in NaOH allows processing of 1,2-dichloroethane and 1,1,2-trichloroethane into vinylidene chloride with up to 70% yield, and vinyl chloride with up to 28% yield, reducing the amount of incinerated chlororganic waste by 2-5 times (Figure 5). The resulting economic effect at “Carpathian-Petrochemical Ltd.” would be about 2.6 M US dollars per year.

At the third stage of this work, polymerization of obtained VC, VDC, and other unsaturated OCW compounds was performed right after alkaline dehydrochlorination, without separation and long-term storage, which reduces installation cost and improves the entire production process safety (Kurta et al., 2007). VC and VDC copolymerization with unsaturated  $\text{C}_5\text{-C}_9$  fraction inside OCW is suggested. This fraction forms from diesel fuel pyrolysis as a side product of olefins production facilities in Kalush, Ukraine.  $\text{C}_5\text{-C}_9$  fraction contains significant amount of valuable monomers: 20-25% isoprene, 20-25% cyclopentadiene, and 10-14% of other pentadienes.  $\text{AlCl}_3$  was used as a catalyst here. Polymerization was carried out in the 15-70 °C temperature range by changing the OCW,  $\text{C}_5\text{-C}_9$ , and solvent components volume ratio. Chemical interaction of VC and VDC copolymers with  $\text{AlCl}_3$  leads to the micro-ions formation.  $\text{C}_5\text{-C}_9$  fraction mostly consists of olefins and dienes and micro-ions can cause polymerization of them. In addition to polymerization and co-polymerization of olefins, ion grafting of isoprene, pentadiene, and n-pentane of VC and VDC copolymers could occur. Grafted polymers were obtained in the environment of organic inert solvent (xylene, toluene, or OCW were used here). VC and VDC copolymers can form in the following way:



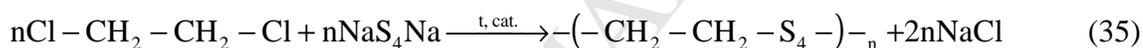
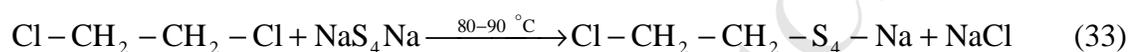
Isoprene grafting can happen in the following way:



The effects of temperature and  $\text{AlCl}_3$  catalyst on the conversion and yield of VC, VDC, and  $\text{C}_5\text{-C}_9$  fraction in the copolymerization are shown in Figure 6. Increasing the temperature from 25 °C to 65 °C slightly improves the copolymerization reaction rate. In this temperature range, products conversion increases from 84% to 87% due to the ionic character of the OCW and the  $\text{C}_5\text{-C}_9$  fraction copolymerization reaction.  $\text{AlCl}_3$  catalyst has a positive effect on the copolymer yield, as seen in Figure 6. Thus,  $\text{AlCl}_3$  catalyst can be recommended for OCW recycling (Kurta et al., 2007). This method allows producing inexpensive and nontoxic polymeric products from waste, reducing the amount of OCW burned by 15%. Such polymeric products can be used as components of anti-corrosive waterproofing coatings (Ramachandran et al., 2002).

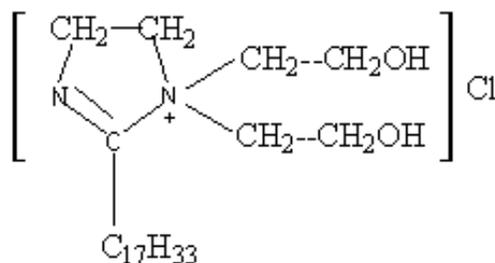
In the fourth stage of this research, a new method of OCW recycling is introduced. This method is based on OCW polycondensation with sodium tetrasulfide ( $\text{Na}_2\text{S}_2$ ,  $\text{Na}_2\text{S}_4$ ) solution, in the presence of phase transfer catalysts (Kurta et al., 2007). Sulfide-containing alkalines from olefins production waste were used, instead of water, for preparing tetrasulfides solutions. This waste formed in the ethylene-propylene production during alkaline washing of pyrogas from  $\text{H}_2\text{S}$  and  $\text{CO}_2$  acid gases. Sulfide-

containing alkalines include 12-20% of sodium sulfide and 4-6% of sodium hydroxide. There are no effective recycling methods for the sulphide-containing alkalines. Seven thousand t/y of these alkalines forms during 250,000 t/y ethylene-propylene production in Kalush, Ukraine (Ramachandran et al., 2002). During recycling (polycondensation) of OCW, using 1,2-EDC and sodium sulfide as examples, the following reactions ensure the polymer chain growth:



OCW, sodium, and potassium sulfides polycondensation occurs by  $S_N2$  nucleophilic substitution of chlorine in OCW by polysulfide and sulfide ions. Nucleophilic substitution of chlorine atoms in alkane derivatives occurs without complications at low temperatures and atmospheric pressure (Araneo et al., 1996). At the same time, ethylene's chlorine-substituted and aromatic compounds, included in OCW, are less active in the nucleophilic substitution reaction. Thus, for complete OCW neutralization under mild conditions, it is necessary to use transfer catalyst. Derivatives of quaternary ammonium salts are widely used as catalysts in this case (Kurta et al., 2007). Non-equilibrium reaction occurs at the phase boundaries. This process runs only during intensive mixing with CaO and Ca(OH)<sub>2</sub> dispersant at 300-450 rpm, or in the presence of highly-dispersed silica (SiO<sub>2</sub>), which allows to increase the contact surface,

or in the presence of an interphase transfer catalysts Imidostat O (heksadetsyl-methylene-amino dyetanol ammonium chloride) (Kurta, 2012).



As a result of the 1-4 hours reaction, water-insoluble polycondensation products in the form of solid or viscous sulfur-containing oligomers and polymers suspensions form (Kurta et al., 2009).

Based on experimental results in Figure 7, the amount of OCW components (1,2-EDC, 1,1,2-TCE) was reduced, and simultaneously the amount and yield of Thiokol polymers were increased in the reaction mixture by 60%. It can be also seen that the total OCW conversion in this experiment reached 55-98%. This can be explained by the optimal ratio of all reaction components. Thiokol macromolecular compounds' output reached 60% (Kurta, 2009). At the same time, sodium sulfide in the sulfide-alkaline is almost used up, decreasing from 20% to 1% in 8 hours in Figure 8. This optimized approach is a good example of waste-free production.

This OCW conversion allowed obtaining sulfur-containing polymer products with up to 50% yield. These products can be used as modifiers for asphalt and bitumen compositions, increasing their frost resistance (Ramachandran et al., 2002). The economic effect of using this method at "Carpathian-Petrochemical Ltd." is estimated at 14.5 M US dollars per year savings.

Integrated application of the four described methods of comprehensive OCW processing allows reducing the amount of burned byproducts and recycles them by 80-90%. The estimated total economic effect of using all the methods described in this paper just by one “Carpathian-Petrochemical Ltd.” production facility could reach 21.6 M US dollars per year.

## 5. Conclusions

The following conclusions can be drawn:

1. Economic inefficiencies and environmental hazards of the OCW burning method, currently used in industrial production of chlororganic products, were explained. OCW disposal by burning results in 1.5 M US dollars per year losses for just one production facility.
2. Chlorination of unsaturated OCW increased 1,2-dichloroethane content by 9-15%, and reduced 1,2-dichloroethane losses when burned.
3. Process conditions of alkaline dehydrochlorination were optimized using a freshly prepared  $\text{Ca(OH)}_2$  suspension in NaOH. This allowed processing of 1,2-dichloroethane and 1,1,2-trichloroethane into vinyl chloride and vinylidene chloride (yield of 28% and 70%, respectively), reducing the amount of incinerated chlororganic waste by 2-5 times. The estimated economic effect of using this method at only one facility is about 2.6 M US dollars per year.

4. A new method of OCW processing by polymerization and copolymerization with unsaturated C<sub>5</sub>-C<sub>9</sub> monomers fraction is proposed. It allows obtaining inexpensive and nontoxic polymeric products out of waste. Such polymeric products can be used as anti-corrosive waterproofing coatings components and can reduce the amount of OCW burned by 15%.

5. Joint utilization with sulphide-containing alkalines makes it possible to process concentrated OCW liquids. 55-98% OCW conversion allowed obtaining sulfur-containing polymer products with 26-50% yield. These products can be used as modifiers for asphalt and bitumen compositions, increasing frost resistance. The economic effect of using the proposed method only by one company is estimated at 14.5 M US dollars per year savings.

6. Integrated application of the four proposed methods of complex OCW processing allows reducing the number of byproducts that are burned and recycles them by 80-90%. The estimated total economic effect of using all the methods described in this paper just by one production facility could reach 21.6 M US dollars per year.

## References

- Al-Hajri, R., Chadwick, D., Single-stage oxychlorination of ethanol to ethylene dichloride using a dual-catalyst bed. *Applied Catalysis A: General* 388 (2010) 96–101.
- Allen, J.A., Clark, A.J., *Review of Pure and Applied Chemistry*. Royal Australian Chemical Institute, 1971.
- Araneo, S., Arrigoni, R., Bjøsyik, H.-R., Fontana, F., Liguori, L., Minisci, F., Recupero, F., New free-radical chain processes involving substitution of vinyl and aryl chlorides by alkanes, alkenes, esters and ethers, *Tetrahedron Lett.* 37 (1996) 6897-6900.
- Bae, J.W., Lee, J.S., Lee, K.H., Lee, B., Yang, D.J., A novel method of CCl<sub>4</sub> disposal by disproportionation with CH<sub>4</sub> over Pt on various supports, *Chem. Lett.* 3 (2001) 264-265.
- Beesley, T.E., Buglio, B., Scott, R.P.W., *Quantitative Chromatographic Analysis*, Marcel Dekker INC, New York, Basel, 2001.
- Borruso, A.V., CEH Product Review. Vinyl Chloride Monomer (VCM), *Chemical Economics Handbook*, SRI Consulting, Zürich, 2006.
- Conte, M., Carley, A.F., Heirene, C., Willock, D.J., Johnston, P., Herzing, A.A., Kiely, C.J., Hutchings, G.J., Hydrochlorination of acetylene using a supported gold catalyst: A study of the reaction mechanism. *J. of Catalysis* 250 (2007) 231–239.

Cowfer, J.A., Magistro, A.J., Vinyl chloride and poly(vinyl chloride), Kirk Othmer Encycl. 23 (1983) 865.

Ding, J., Hua, W., Zhang, H., Lou, Y., The development and application of two chlorine recycling technologies in polyurethane industry, Journal of Cleaner Production 41 (2013) 97-104.

Hazel, R.H., Solving hazardous waste problems in Missouri using the EPA mobile incinerator, Chemosphere 19 (1989) 557-560.

Hung, S.L., Pfefferle, L.D., Methyl chloride and methylene chloride incineration in a catalytically stabilized thermal combustor, Environ. Sci. Technol. 23 (1989) 1085-1091.

Kurta, S.A., Mykytyn, I.M., Pronik, A.D., Ukraine Patent No. 24,933. Ukrainian Institute of Industrial Property, Kyiv, 2006, (Ukraine).

Kurta, S.A., Zakarzhevsky, A., Kurta, M., Utilization of the chlororganic waste by method of their catalytic copolymerization, Polimery (Poland) 1 (2007) 51-55 (in English).

Kurta, S.A., Zakarzhevsky, A., Kurta, O. Voronych, O., Ivanyshak, N., Polycondensation of sulfid containing and chlororganic waste at the surface interface, Phys. Chem. Solids 3 (2009) 696-701, (Ukraine).

Kurta, S.A., Investigating active centers of industrial catalysts for the oxidative chlorination of ethylene on a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, *Catal. in Ind.* 3 (2011) 136-143,(Russia)

Kurta, M.S., Environmental and Energy Saving Technologies of Vinyl Chloride Production, M.S. Thesis, University of South Florida, Tampa, 2012.

Lakshmanan, A., Rooney, W.C., Biegler, L.T., A case study for reactor network synthesis: the vinyl chloride process. *Comput. and Chem. Eng.* 23 (1999) 479–495.

Lamberti, C., Prestipino, C., Capello, L., Bordiga, S., Zecchina, A., Spoto, G., Diaz Moreno, S., Marsella, A., Cremaschi, B., Garilli, M., Vidotto, S., Leofanti, G., The CuCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst investigated in interaction with reagents, *Int. J. Mol. Sci.* 2 (2001) 230-245.

Manning, M.P., Fluid bed catalytic oxidation: An underdeveloped hazardous waste disposal technology, *J. Hazard. Waste* 1 (1984) 41-65.

McPherson, R.W., Starks, C.M., Fryar, G.J., Vinyl chloride monomer... What you should know. *Hydrocarb. Process* 75 (1979) 75-85.

Mitoma, Y., Nagashima, S., Simion, S., Simion, A.M., Yamada, Y., Mimura, K., Ishimoto, K., Tashiro, M., Dehalogenation of aromatic halides using metallic calcium in ethanol, *Environ. Sci. Technol.* 35 (2001) 4145-4148.

Naworski, J.S. Evil, E.S. *Applied Industrial Catalysis*. Academic Press, New York, 1983.

Ramachandran, V.S., Paroli, R.M. Beaudoin, J.J. Delgado, A.H., 13 – Introduction to organic construction materials, Handbook of Thermal Analysis of Construction Materials, Institute for Research in Construction National Research Council of Canada Ottawa, Ontario, Canada, 2002, pp. 531–577.

Papp, R., Organochlorine waste management, Pure Appl. Chem. 68 (1996) 1801–1808.

The United Nations Environment Programme. International Environmental Governance: Multilateral Environmental Agreements, 2001.

[www.gdrc.org/uem/mea/un-mea-full.pdf](http://www.gdrc.org/uem/mea/un-mea-full.pdf) last accessed on 2/10/2013

Thornton, J., Environmental Impacts of Polyvinyl Chloride Building Materials. Healthy Building Network, Washington, D.C., 2002.

Zakarzhevsky, A., Kurta, S.A., Research on the rectification process of chlororganic waste 1,2-dihloretana and vinyl chloride, East. Eur. J. Adv. Technol. 6 (2006) 41-45, (Ukraine).

### Figure captions

Fig. 1. Experimental equipment setup for alkaline dehydrochlorination of OCW and their separation: 1- Claisen flask placed in the thermostat; 2- mixer; 3- thermometer; 4- direct condenser; 5- allonge; 6- receivers for VC and VDC; 7-vacuum; 8-manometer; 9- thermostat.

Fig. 2. Reactor autoclave assembly schematics for the copolymerization of the products of alkaline OCW dehydrochlorination with the C5-C9 fraction: 1-hood; 2- pulley reactor; 3-V belt; 4-seal; 5-manometer; 6-thermometer; 7-top cover of the reactor; 8-nipple; 9-support; 10- heat carrier output; 11-thermostat motor; 12-reactor autoclave with the thermal jacket; 13-heat carrier input; 14-thermostat remote control; 15-flange outlet; 16-faucet; 17-thermostat; 18-mixer drive motor of the housing; 19-connection for the reactants; 20-engine speed regulator.

Fig. 3. OCW unsaturated compounds concentration change inside the rectification column after chlorination at 60 °C, 1:10 OCW to Cl<sub>2</sub> molar ratio, and Fe –catalyst, 1.5 atm pressure.

Fig. 4. EDC concentration change in OCW inside the rectification column after chlorination at 60 °C, 1:10 OCW to Cl<sub>2</sub> molar ratio, and Fe -catalyst.

Fig. 5. VC and VDC yield dependence on NaOH concentration in the dehydrochlorinated OCW mixture. (75 °C, 2 hours, 300 rpm, NaOH:Ca(OH)<sub>2</sub> = 1:2).

Fig. 6. OCW conversion rate, insoluble OCW copolymer and C5-C9 fraction yield temperature dependence. (6% AlCl<sub>3</sub>, 4 hours).

Fig. 7. OCW components (1,2-EDC, 1,1,2-TCE) concentration and thiokol polymers yield during polycondensation with sulfides, (83-90 °C, OCW:Na<sub>2</sub>S<sub>4</sub>:sulfide-containing alkaline = 1:2:1; CaO-5%; cat-0.5wt.% 1H-Imidazolium).

Fig. 8. Sulphide-containing alkalines concentration change during interaction with OCW. (83-90°C; OCW:Na<sub>2</sub>S<sub>4</sub>:sulphide-containing alkaline = 1:2:1; CaO-5%; cat-0.5wt.% - Imidostat-O, 1 atm pressure)

Table 1

OCW chemical composition for EDC and VC production.

OCW components	Component content, wt.%	Hazard class	Maximum allowable concentration in air, mg/m <sup>3</sup>
Vinyl chloride monomer	0.0003	1	1
Allyl chloride (1- chloropropylene)	0.0039	1	0.3
Trans 1,2 DCE	0.0009	-	-
Carbon tetrachloride ( tetrachloromethane)	0.0215	2	20
Benzene	0.01	2	15
Chloroform (trichloromethane)	0.0134	2	20
1,1,2-trichloroethylene	0.019	2	10
1,2- dichloroethane (EDC)	16.4 - 35	2	10
Tetrachlorethylen	0.418 - 0.9	2	10
1,2,3-trichloroethane	36.61 - 40	2	20
1,1,2,2-tetrachloroethane	2.034 - 4	2	5
Ethylene chlorohydrin	0.444 - 0.5	1	0.5
1,1-dichloroethane	0.16 - 1	2	10
Unidentified OCW	43.865 - 19	1-2	-
Total	100	2	10

Table 2

Physical properties of the C<sub>5</sub>-C<sub>9</sub> fraction

Indicator name	Value
Fractional composition: Boiling temperature at the beginning Temperature at the end of the boil	>30 °C <200 °C
Mass concentration of the fact. resins	<500/100 mg/cm <sup>3</sup>
Chlorine mass fraction	<0.002%
Sulfur mass fraction	<0.1%
Density	617-730 kg/m <sup>3</sup>
Bromine number	100-180 Br <sub>2</sub> / 100 g resin
Flash point combustion	40 °C
Interval, spontaneous combustion of vapor in air	1.48-8vol.%
Maximum permissible concentration in air	100 mg/m <sup>3</sup>

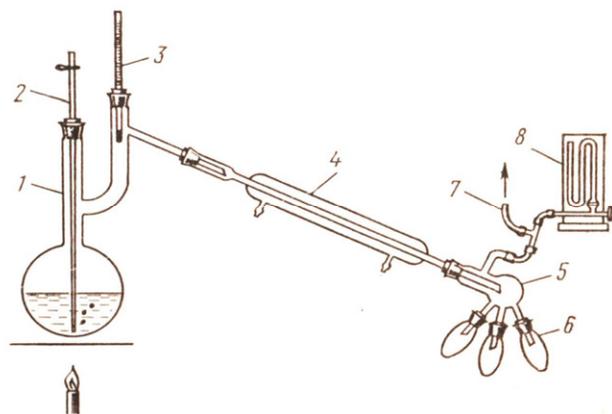


Fig. 1

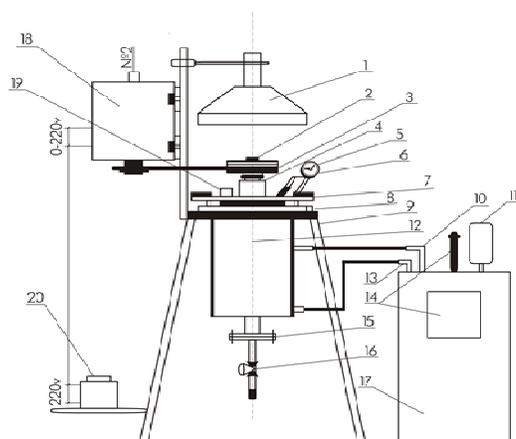


Fig. 2

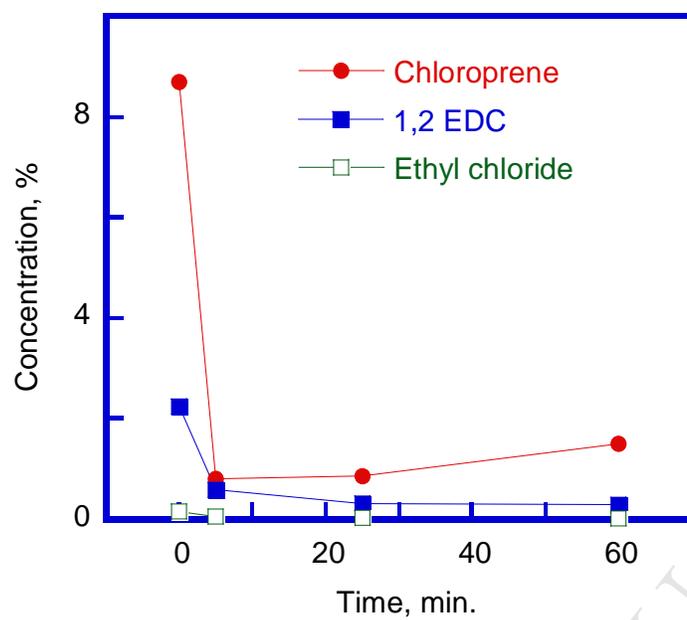


Fig. 3

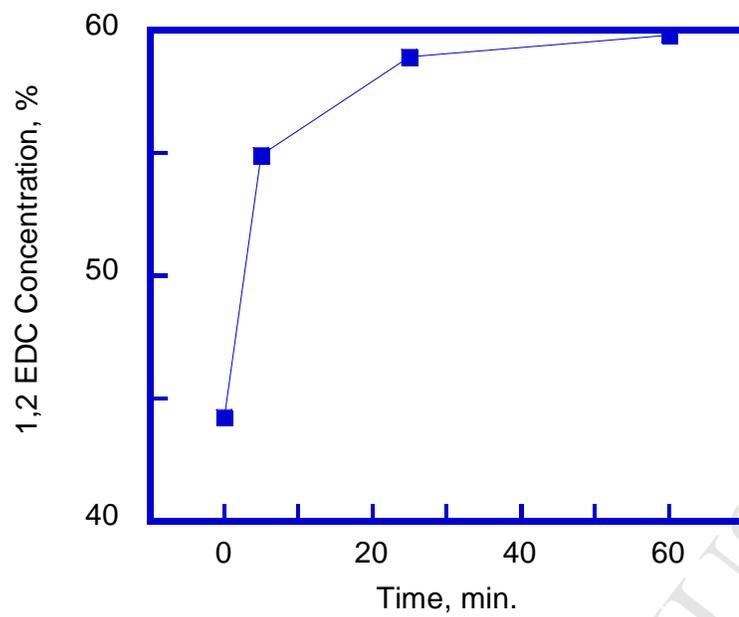


Fig. 4

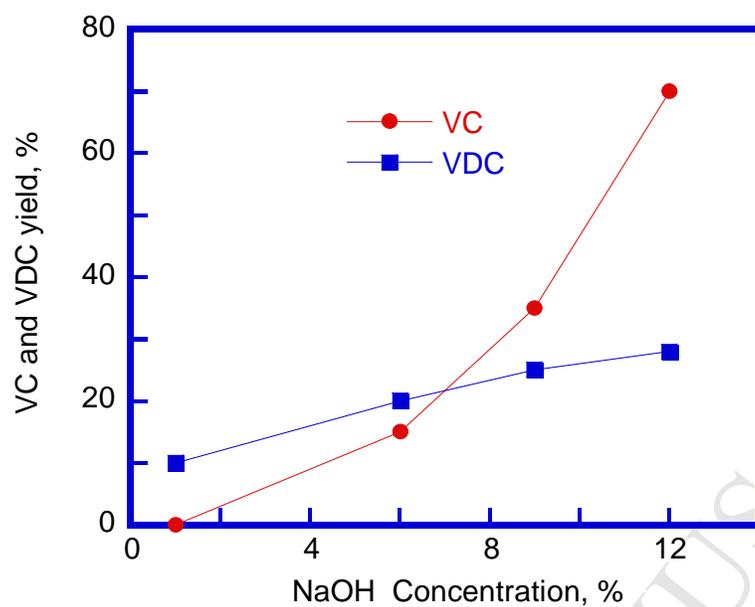


Fig. 5

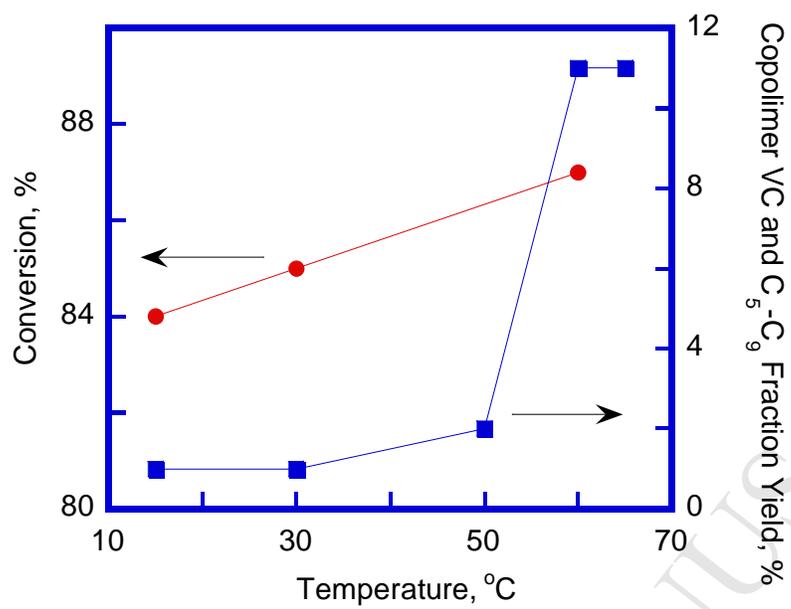


Fig. 6

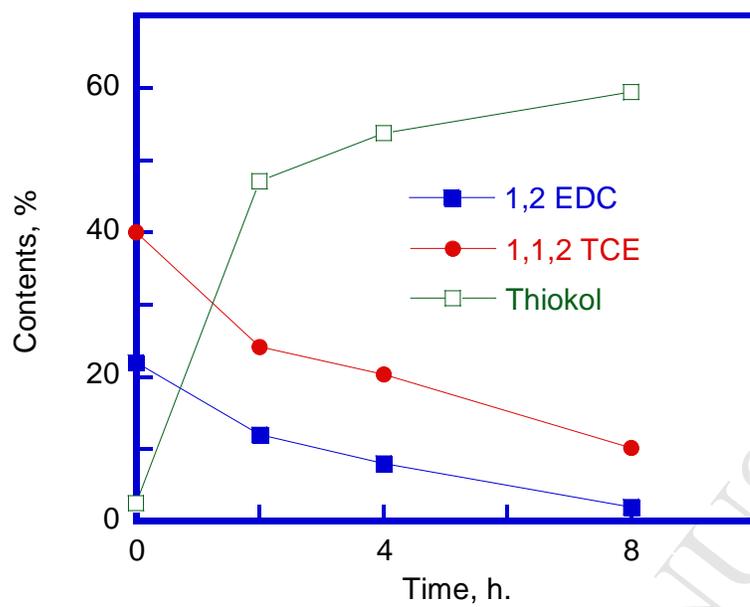


Fig. 7

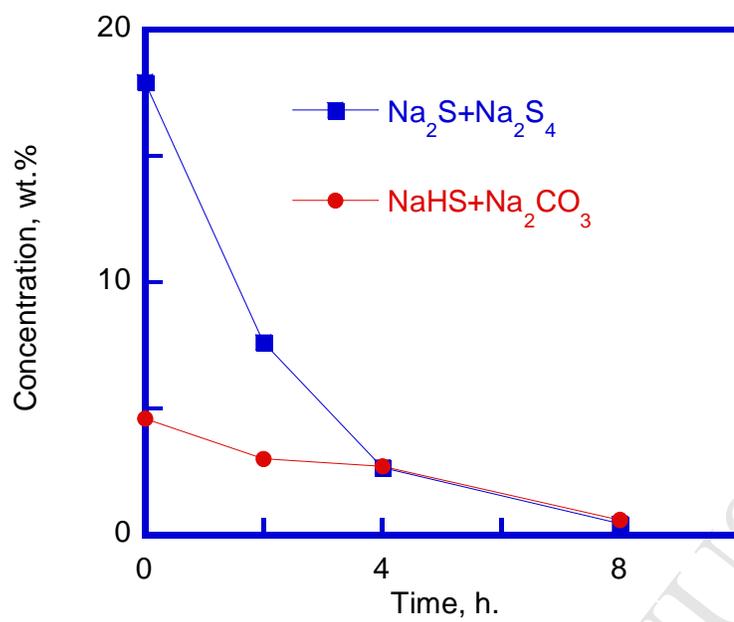


Fig. 8