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Pyrolysis of 1, 2-dichloropropane

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Pyrolysis of 1, 2-dichloropropane

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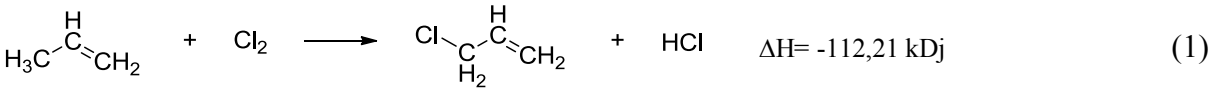
Abstract. Process of pyrolysis 1, 2 dichloropropane to a allyl chloride have been studied. The reaction was carried out both homogeneously without a catalyst and using catalysts: quartz, waterless $CaCl_2$; 15% mass. Cu/SiO_2, 15% mass. $CaCl_2/Al_2O_3$. It is shown that at 1, 2 dichloropropane conversion 15-40 % main pyrolysis byproducts were DCP is (cys-, trans-) 1-CP and 2-CP with trans-1-CP in most. At that parameters of pyrolysis, it is possible to achieve productivity by an allyl chloride 0.5-0.7 g/(ml·h).

1. Introduction

Allyl chloride (3-chloro-1-propene, 3-CP) used for production epichlorohydrin, glycerol, allyl alcohol, allyl ethers, allylamine, cyclopropane, allyl sucrose, drugs and insecticides [1]. Allyl chloride carried out in two ways [1, 2]. The first method consist of propylene chlorination at 450-550 °C and molar ratio propylene to chlorine 5/1, allyl chloride yield by chlorine 80%.



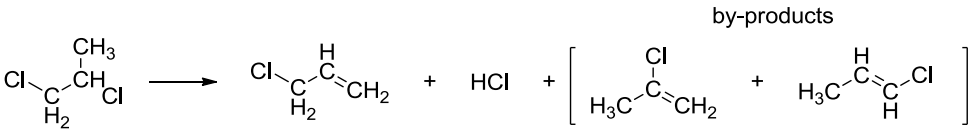
(1)

Second way connected with high temperature 1, 2-dichloropropane (DCP) dehydrohalogenation (520-540 °C):

(2)

Allylchloride yield achieve to 50-70 %.

According to [2, 3] thermal pyrolysis DCP in addition to HCl delivering and 3-CP formation have place monochloropropene by-product:



(3)

In the works [4, 5] for 1,2-dichloropropane thermal pyrolysis used catalysts. DCP is obtained as a by-product of syntheses. The development new route for transformation DCP play important role to reduce the environmental load of persistent organic pollutants (POP).

2. Experimental Part

Pyrolysis process studied at 400-580 ºC and contact time between 2-8 sec. The reaction was carried out both homogeneously without a catalyst and using catalysts: quartz, waterless $CaCl_2$; 15% mass. Cu/SiO_2, 15% mass. $CaCl_2/ Al_2O_3$.

DCP dehydrochlorinationn was carried out in a tube, quartz reactor with 12 mm diameter size. Liquid phase analysis by GC «Chromatech-Crystal 5000.2» (by JSC SDO CHROMATEC) equipment with FID detection, capillary column ZB-Wax (by Zebron), 30m×0,25mm×0,25mkm, temperature increase from 40 °C, 2 °C /min to 70 °C, 20 °C /min to 220 °C. Gas phase analysis after HCl absorption by 0.1 M water solution NaOH carried out according to [6]. GC "Crystal 5000.1" with two TCD and FID detectors was used for the analysis. The following chromatography columns were used to separate the gas mixture. First, a packed column 4 m long with a sorbent NaX (60/80 mesh) (by JSC SDO CHROMATEC) to separate and determine hydrogen, oxygen, nitrogen, methane and carbon monoxide (eluent Ar). Second, 1.5 m packed column with Carbosieve S-II sorbent (60/80 mesh) (by JSC SDO CHROMATEC) for detecting and calculating the concentration of carbon dioxide (eluent He). Third, 50 m capillary column HP-PLOT Al_2O_3 (KCl) (by Agilent) for separation and determination of hydrocarbons C_1-C_5. Column temperature was 80 °C.

The catalytic parameters of the process were calculated by the equation (n – amount of a substance, mol; m – mass of a substance, g: t – time of production, h; V_{cat} – catalyst volume, ml):

Conversion of 1,2-dichloropropane

$$X_{1,2-dichloropropane} = \frac{n^{in}_{1,2-dichloropropane} - n^{out}_{1,2-dichloropropane}}{n^{in}_{1,2-dichloropropane}} \times 100\%$$

Selectivity toward 3-chloro-1propene

$$S_{3-chloro-1-propene} = \frac{n^{out}_{3-chloro-1propene}}{n^{in}_{1,2-dichloropropane} - n^{out}_{1,2-dichloropropane}} \times 100\%$$

Yield toward 3-chloro-1propene

$$Y_{3-chloro-1propene} = \frac{n^{out}_{3-chloro-1propene}}{n^{in}_{1,2-dichloropropane}} \times 100\% = \frac{X_{1,2-dichloropropane} \times S_{3-chloro-1-propene}}{100\%}$$

Productivity toward 3-chloro-1propene

$$P_{3-chloro-1propene} = \frac{m^{out}_{3-chloro-1propene}}{t \times V_{cat}}$$

3. Results and Discussion

Investigations of the pyrolysis of 1,2-dichloropropane at empty quartz reactor showed in case at 550 ºC when contact time grows (at changing DCP loading in a reactor) have place increasing conversion DCP and decreasing selectivity toward 3 – CP (figure 1). Selectivity toward 3-CP more by 30 % than theoretical calculating by thermodynamic methods. The process kinetic factors ruled selectivity toward 3-DCP.

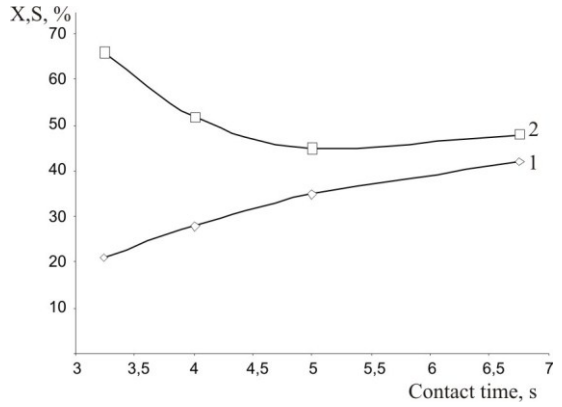


Figure 1. Conversion DCP (1) and selectivity (2) toward 3-CP on contact time at 550 ºC in empty reactor.

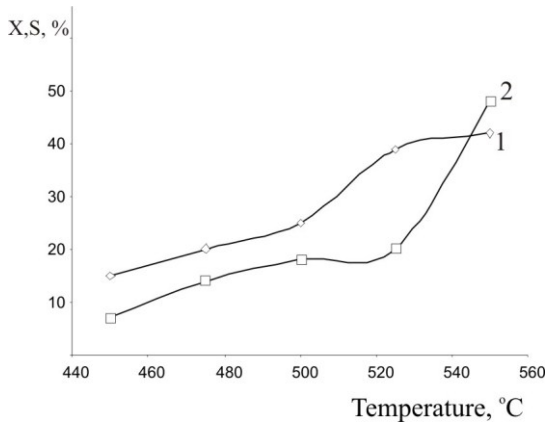


Figure 2. Conversion DCP (1) and selectivity (2) toward 3-CP on process temperature at τ= 6.75 sec in empty reactor.

According to figure 2 temperature increasing at constant contact time τ= 6.75 sec, lead to increasing conversion DCP and selectivity toward the target product. 3-CP's yield at 550 ºC near to 20%.

Pyrolysis DCP on waterless $CaCl_2$ inside a quartz reactor showed in case τ= 6.75 sec, selectivity toward 3-CP and conversion DCP lower than empty reactor with same (figure 3). Temperature increasing leaded to higher selectivity and conversion, but lower than for empty reactor.

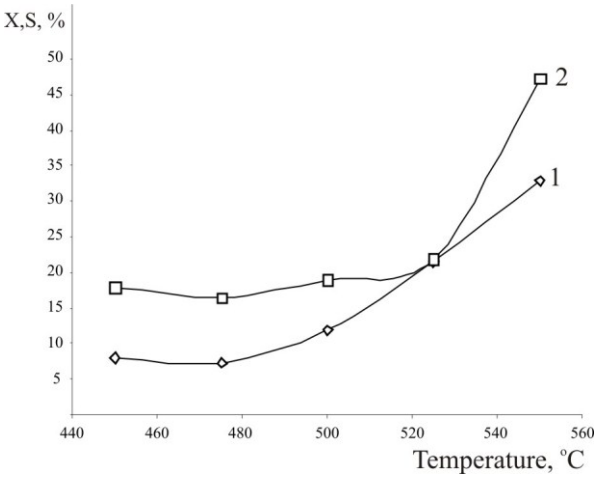


Figure 3. Conversion DCP (1) and selectivity (2) toward 3-CP on process temperature at τ= 6,75 sec. (waterless $CaCl_2$).

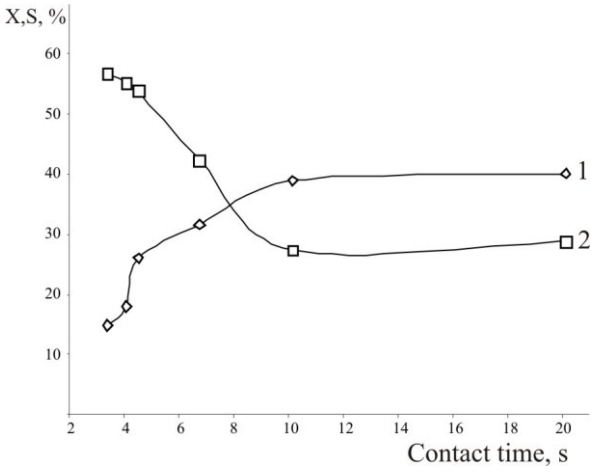


Figure 4. Conversion DCP (1) and selectivity (2) toward 3-CP on contact time at 550 ºC. (waterless $CaCl_2$).

Time contact rising from 3.38 sec to 10 sec in case $CaCl_2$ lead to increase conversion and decrease selectivity toward the target product (figure 4).

Pyrolysis DCP on 15% mass. Cu/SiO_2 inside a quartz reactor showed higher conversion relative to $CaCl_2$. Copper supported on silica gel has high catalytic activity toward byproducts. At 375 ºC conversion of DCP is about 20%, but selectivity for allyl chloride does not exceed 8%. Temperature increasing lead to rise conversion of DCP, and lowering selectivity (figure 5). The main products DCP conversion is allene and propine. Also, have place cracking's products: methane, ethylene, athethylene, hydrogen.

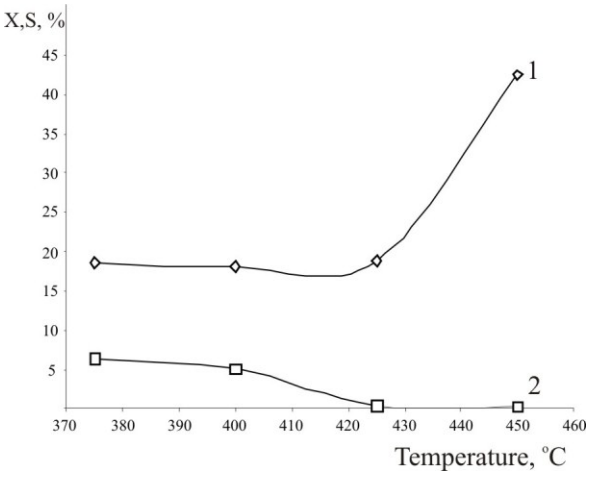


Figure 5. Conversion DCP (1) and selectivity (2) toward 3-CP on process temperature at τ= 6.75 sec. (15% mass. Cu/SiO_2).

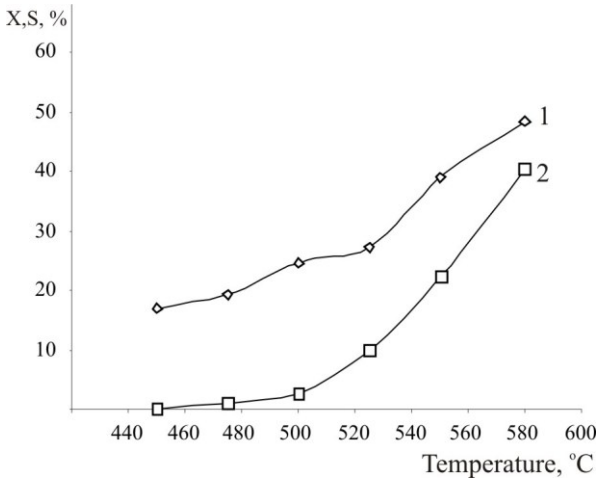


Figure 6. Conversion DCP (1) and selectivity (2) toward 3-CP on process temperature at τ= 2.2 sec. (grit quartz).

Figure 6 reflect temperature influence on 3-CP selectivity in case τ=2.2 sec and reactor filled with grit quartz. In that case, the behavior trend of selectivity and conversion is analogous to behavior these parameters for empty reactor. However, increasing conversion and selectivity with temperature increasing have place at lower contact time than for empty reactor and higher productivity per unit volume of reactor (table 1).

Use as a backfill $CaCl_2/Al_2O_3$ showed catalytic activity toward cracking reactions that lead to decreasing selectivity toward 3-CP formation. Main products were: methane, ethylene, athethylene, hydrogen. Over time, the surface of $CaCl_2/Al_2O_3$ formed carbon and have placed 3-CP formation with lower selectivity than in case grit quartz (figure 7).

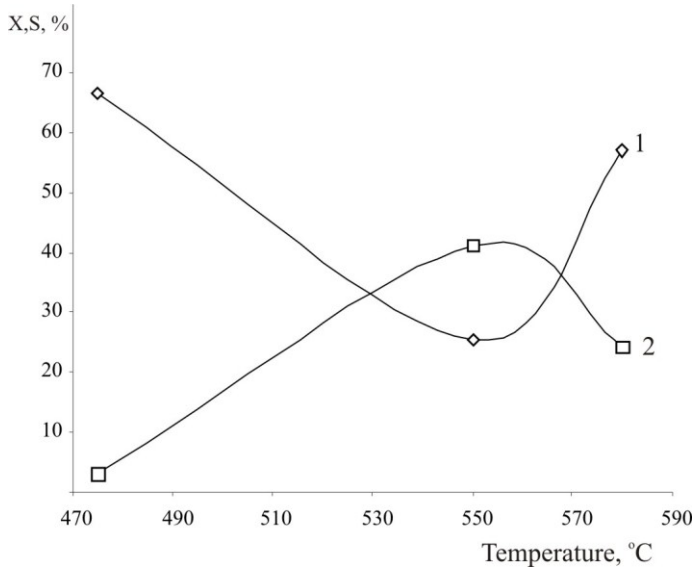


Figure 7. Conversion DCP (1) and selectivity (2) toward 3-CP on process temperature at τ= 3.38 sec. ($CaCl_2/Al_2O_3$).

As a result of our research work, we were able to determine the optimum conditions for the achievability of high productivity toward 3-CP formation per reactor's volume (P, g / ml • h). See the results in table 1.

Table 1. Optimal contact time and temperature for DCP pyrolisis, when reactor's filling is change. DCP conversion, 3-CP selectivity, yield toward 3-CP and productivity.

No	Filling type	τ, c	T, ºC	X_{DCP}, %	$S_{3\text{-}CP}$, %	$Y_{3\text{-}CP}$, %	P, g/ml·h
1	Empty	6.75	550	42.0	48.1	20.2	0.37
2	$CaCl_2$	6.75	550	26.1	54.0	14.1	0.26
3	15% mass. Cu/SiO_2	6.75	375	15.1	9.3	1.25	0.023
4	Quartz	3.38	580	48.5	40.1	19.6	0.71
5	$CaCl_2/Al_2O_3$	3.38	580	57.0	24.1	14.1	0.505

X_{DCP} – conversion of 1,2-dichloropropane
$S_{3\text{-}CP}$ – selectivity on a allyl chloride
$Y_{3\text{-}CP}$ – yield on a allyl chloride
P – productivity on a allyl chloride

4. Conclusion

At DCP conversion 15-40 % main pyrolysis byproducts were cys-1-CP, trans-1-CP and 2-CP. Due to pyrolysis process formed solid chlorinated carbon. This carbon increases selectivity and allyl chloride yield. The optimum temperature range for pyrolysis in a quartz reactor is 550-580 ºC at 3-5 s contact time, which makes it possible to achieve a yield of allyl chloride of 20-25% per pass. At that parameters possible to achieve productivity toward an allyl chloride 0.5-0.7 g/(ml·h).

References

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