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(54) Title: PROCESS FOR THE PRODUCTION OF VINYL CHLORIDE

(57) Abstract: The present invention relates to a process for the production of vinyl chloride by thermal cracking of 1,2-dichloroethane (EDC) to form a reaction mixture containing vinyl chloride (VCM), hydrogen chloride (HCl), unconverted 1,2-dichloroethane, the impurity 1,3butadiene and other by-products in which the troublesome by-product 1,3-butadiene is removed. The reaction mixture is quenched and said vinyl chloride is separated from said mixture. Said 1,3-butadiene is removed from said quenched mixture prior to said vinyl chloride separation by reacting with chlorine added to said mixture after addition of a butadiene reduction agent to said mixture. The butadiene reduction agent is selected from the classes of compounds known to or expected to act as radical scavengers. The butadiene reduction agent is an aromatic compound selected from the groups consisting of aromatics with one or more oxygen attached to the ring. Preferably, said butadiene reduction agent is a para-substituted phenol as 4-methoxyphenol, 4-cresol or hydroquinone.

"Process for the production of vinyl chloride"

The present invention relates to an improved process for the production of vinyl chloride by thermal cracking of 1,2-dichloroethane, in which the by-product 1,3-butadiene is chlorinated in the presence of a butadiene reduction agent.

Vinyl chloride (VCM) is manufactured on an industrial scale by thermal cracking of 1,2-dichloroethane (or ethane dichloride (EDC)). The typical temperature range is 500-550°C, the typical pressure is 10-30 bara and the typical EDC conversion is 50-70%. The main by-product in EDC cracking is HCl. Minor by-products consist of a range of chlorinated hydrocarbons with one or more C-atoms in the chain; for example monovinylacetylene, chloroprene, 1,3-butadiene, trichlorethane, chlorinated C_4's. A simplified process scheme for EDC cracking to VCM is shown in Fig. 1. After the cracking unit 1, the product stream is quenched 2 and the products are separated by distillation. The separation train typically consists of three columns; the HCl column 3 which removes the major part of the HCl 6, the VCM column 4 which removes unconverted EDC and the heavier by-products 7, and finally the HCl stripper which removes traces of HCl 8 from VCM 9. Unconverted EDC with the heavy by-products 7 might be treated in a separate vessel with chlorine to reduce the content of chloroprene before the stream is purified and returned to the cracking unit 1. This is not included in Fig. 1. In this process, 1,3-butadiene (hereafter denoted butadiene) is especially troublesome as the boiling point is close to VCM and butadiene tends to follow VCM in the distillation trains. The major use of VCM is in the production of PVC (polyvinyl chloride), and butadiene is an undesired component in the polymerisation process. Thus, the butadiene content in the VCM product stream must be low when VCM is used for PVC production (spec 8 ppm for traded VCM). In vinyl chloride production there is an economic advantage of increasing the EDC conversion per-pass in the reactor as this among other factors enhances the energy efficiency of the process and reduces the utility cost per metric ton VCM produced. However, as is known to those skilled in the art, increasing EDC conversion inherently increases the yield of butadiene, which ends up in the VCM product stream. In order to take advantage of higher EDC conversion, it is crucial to find methods that reduce the butadiene level in the VCM product stream.

One possible approach for removal of butadiene from the VCM product stream is to convert it to a by-product with a higher boiling point, in such a way that it follows the EDC and the heavier by-products stream in the separation train. Chlorination, hydrochlorination, hydrogenation and polymerisation are all reported methods for this purpose. All methods except the first require a catalyst to proceed at a practical rate. Catalytic processes generally require more advanced reactor engineering as well as maintenance due to catalyst deactivation with time. Removal of metals from the catalyst is hard to avoid, which may create problems in downstream equipment. Therefore, chlorination has an advantage over the other methods in terms of cost efficiency and reliability. The chlorine feed is available in the VCM plant, and the reaction does not generate products that are not already present in the process streams. The main challenge, however, is to find conditions in the VCM plant where chlorine selectively reacts with butadiene, which typically is present in levels of less than 100 ppm in the cracked process stream. It is generally known that chlorine also reacts with VCM, as well as other by-products such as monovinylacetylene and chloroprene. Depending on the concentrations of these compounds and the process conditions, the undesired side reactions will consume some of the chlorine added to the stream, which necessitates a chlorine/butadiene-ratio far above 1. VCM is reacted with chlorine into 1,1,2-trichloroethane (hereafter denoted TCE), resulting in a loss in the yield of VCM and a production of the undesired product TCE, which has a negative effect on the process economics. Although VCM loss through TCE formation is undesirable, some TCE formation may be far outweighed by the positive economic effects of allowing an increase in EDC conversion in the cracker. The chlorination of chloroprene is undesired with respect to chlorine consumption and the selectivity towards butadiene removal. Furthermore, chloroprene in the recycled EDC stream is known to increase the rate of coking and fouling in the cracker tubes and the downstream heat exchangers. Some VCM plants reduce the chloroprene content in the recycled EDC after separation from VCM. Thus a reduction in the chloroprene level by chlorination in the cracker tube effluent is considered an advantage, as long as sufficient butadiene reduction is accomplished.

Some of the methods described in the patent literature are more directed towards a reduction in the chloroprene level than a reduction in the butadiene level. There are various modifications proposed to the VCM production plant in order to accomplish the desired chlorination of butadiene. Some methods focus on treatment of the effluent gas from the cracker tubes, whereas others involve actions on the streams between the distillation columns or on the raw VCM produced.

US 3920761 teaches the addition of chlorine to the process stream at any point after the cracking step, but prior to the separation of VCM. A preferred location is the bottom stream from the HCl column. Cl_2 is recommended dissolved in the reaction mixture after the cleavage of EDC. The reaction with chlorine is carried out at a temperature of from –30 to +150°C. It is claimed that chlorine first reacts with butadiene, followed by reaction with monovinylacetylene and chloroprene before attacking VCM, and that a complete conversion of butadiene, 50% conversion of monovinylacetylene and 75% conversion of chloroprene can be achieved before there is any appreciable attack on VCM. If this is the case, the amount of chlorine added to the process can be regulated by the chloroprene content (which is the largest by-product), and in this manner all butadiene will be converted without significant loss of VCM. Chloroprene can be said to be a buffer against the undesired reaction of VCM into TCE. This approach seems very promising, and has been looked into in detail by the inventors of the present invention. The inventors have carried out experiments where the amount of chlorine has been regulated against the chloroprene content representative to their plants. However, the inventors have not been able to document any buffer effect of chloroprene on TCE formation. The example given in US 3920761 documents a high chloroprene content in the feed of 0.47% relative to the unconverted EDC. This concentration is significantly higher than the one present in the inventors' plants (0.1-0.2% relative to unconverted EDC). It is possible that the chloroprene content in the inventors' process stream is too low to achieve the reported buffer effect. In principle, a buffer could be added to obtain the required effect, but the high amount required can be considered impractical as a process solution. The example given in US 3920761 also requires that a considerable fraction of the total EDC stream downstream of the cracker (42%) needs to be mixed with chlorine and recycled to the VCM column, adding considerable extra load to the separation system. Furthermore, the solution according to the invention described in US 3920761 still leaves a significant amount of chloroprene unconverted which has to be treated downstream of the VCM column. If chloroprene cannot be fully converted in the EDC-VCM stream, it would be an advantage to find a solution that enables attack of chlorine only on butadiene. The advantage would be a much smaller recirculation stream of EDC with chlorine. Also, the conversion of chloroprene in EDC would be done in a single step downstream the VCM column, where selective chlorination is easily achieved.

The results obtained by the inventors of the present invention document that the selectivity towards butadiene is highly dependent on temperature and VCM concentration. At low temperatures (20-50°C) and low concentration of VCM in EDC (< 1%), the chlorination of butadiene is very selective and almost 100% conversion of butadiene can be achieved. However, increasing the VCM/EDC ratio to a value corresponding to 55% EDC conversion, and raising the temperature above 50°C has a strong negative influence on the selectivity towards butadiene removal. The added chlorine preferably reacts with VCM into TCE instead of reacting with butadiene or chloroprene. The results, and a suggested explanation, will be documented later in the present patent application. The typical temperature in the process stream from the bottom of the HCl column towards the VCM column is usually well above 50°C and in the range 60-120°C. Thus, one would not expect a significant reduction in the butadiene or chloroprene level by the method disclosed in US 3920761, instead the loss of VCM into TCE will be the dominating reaction.

Other patents of some relevance to the present invention focus on improved catalyst systems for production of chlorinated hydrocarbons by selective addition of Cl_2 to olefins. The aim is to develop catalysts with higher selectivity and that are less corrosive than the $FeCl_3$ catalyst. US 3624169 discloses a method for production of chlorinated products from olefins such as ethylene, propylene and butadiene by addition of Cl_2 in a solvent (typically EDC, dichloropropane, carbontetrachloride). The reaction is carried out at 0-80°C and 0.5-6 bar. In the case of ethylene chlorination, EDC is the solvent and the catalyst improves the selectivity to the desired chlorinated product (EDC) and reduces the yield of the undesired by-product TCE, which results from chlorine substitution on EDC. In the case of butadiene chlorination, tetrachloromethane, which is not reactive towards Cl_2, is used as solvent. The desired reaction is addition of chlorine to butadiene to form dichlorobutenes. The undesired reaction is further addition of chlorine to produce tetrachlorobutanes or substitution to form trichlorobutenes. It is of relevance that the solvents used are unable to add chlorine, meaning that the major component in the solution has a considerably lower reactivity towards chlorine than the olefin. In the present invention one of the major components in the solution is VCM (> 55%). VCM is an olefin with a reactivity much closer to butadiene, but which must not be reacted.

The catalyst in US 3624169 is claimed to increase the selectivity to the desired products. The catalyst is selected from the group consisting of ortho- and meta-substituted phenols, the most effective being m-cresol (3-methylphenol) and resorcinol (1,3-dihydroxybenzene). It is of relevance that the use of para-substituted phenols was excluded as catalyst as the reaction produced significant amounts of TCE (10 to 100 times more) at the given conditions. The catalyst is claimed to be stable at reaction conditions so that the catalytic activity is preserved with time. The considered process stream in US 3624169 consists of one unsaturated hydrocarbon in a saturated hydrocarbon solvent and the desired reaction is addition of chlorine without chlorination of the product or the solvent. The process stream according to the present invention contains more than 50% unsaturated hydrocarbons, and the desired reaction is selective chlorination of an unsaturated hydrocarbon, namely butadiene, which is present in trace levels, with negligible reaction of the other unsaturated components, especially VCM.

In the present invention and in contrast to US 3624169, the ortho- and meta-substituted phenols have lower selectivity to butadiene chlorination than the para-substituted ones which are thus preferred. All phenols give roughly the same amount of TCE (see Table 3 in the present patent application) in contrast to what is shown in US 3624169, in which case 10-100 times more TCE is produced when para-substituted phenol is used as catalyst.

The catalysts in US 3624169 are further claimed to be stable under reaction conditions, whereas the additives used in the present invention are consumed.

US 5177233 concerns use of a ferric phenolate/chlorine complex as catalyst for the direct chlorination of ethylene to EDC.

DE 2754891 discloses a method for reduction of chloroprene in the cracking effluent stream. Chlorine and a hydroxyl-aromatic compound are added to EDC, and the mixture is introduced into the process stream at the bottom of the VCM column. Chlorine is added in surplus to the chloroprene content, and ethylene is thereafter added to the stream in an amount comparable to the surplus chlorine for conversion of chlorine to EDC. The reactions preferably take place around 20-30°C and 0.5-6 bars. Addition of the hydroxyl-aromatic compound (preferably o-, m-cresol) is claimed to have several advantages: Enhanced reduction of the chloroprene content without increasing the formation of TCE as well as an increase in the conversion of ethylene to EDC, being close to 100%. The hydroxyl-aromatic compound is partly chlorinated and follows the unconverted EDC and heavy by-product stream in the separation system. The chlorination reaction in this case is also carried out in a saturated solvent (EDC). The results obtained by the inventors of the present invention show that at low temperature (< 60°C) and in the absence of VCM, the chlorination of chloroprene is fairly easy and selective even without addition of an aromatic compound. The disclosed method does not address butadiene removal since butadiene has been separated from the process stream at the point of implementation; butadiene follows VCM and exits at the top of the VCM distillation column.

In US 3876714 the raw gas from the cracker is cooled to a pressure above 1 bar in order to achieve a gas phase and a liquid phase. Chloroprene and butadiene present in the liquid stream are reacted in a vessel with chlorine. A catalyst such as $FeCl_3$ might be added to the system to aid the chlorination process. The preferred temperature is around 40°C. The method focuses on reduction of chloroprene, but is said to be effective also for butadiene reduction.

A similar approach is taught in US 4760206. Chlorine and $FeCl_3$ catalyst are introduced in the quench column after the cracker. The product gases are quenched with EDC. Chlorine is added in less than stoichiometric amount to butadiene. The $FeCl_3$ catalyst is claimed to be active for both chlorination and polymerisation of butadiene. At a butadiene level below 100 ppm it is claimed that the polymerisation product does not introduce instabilities or problems in the plant operations by fouling or plugging of downstream equipment. However, the risk of negative effects of the polymerisation products as well as the possibility of fouling from species generated over the $FeCl_3$ catalyst are major drawbacks to these approaches.

US 3125607 teaches the addition of Cl_2 into a liquid VCM stream in the temperature range -20°C – 0°C and space time 4 h.

GB 1426677 teaches the use of adding chlorine and a hydrocarbon to the raw VCM in liquid phase in the preferred temperature range 20-60°C. Butadiene is selectively chlorinated. The hydrocarbon added should have a reactivity for chlorination that is higher than VCM, but lower than butadiene. Suitable hydrocarbons are stated to be chloroprene, butenes or monovinylacetylene. In these approaches, the raw VCM-stream must be purified after the treatment with chlorine, which adds cost and complexity to the process.

The main objective of the present invention was to provide an improved process for the production of vinyl chloride by thermal cracking of 1,2-dichloroethane, in which the troublesome by-product 1,3-butadiene is removed.

Another objective of the present invention was to provide an improved process for the production of vinyl chloride by thermal cracking of 1,2-dichloroethane, in which the EDC conversion in the cracking unit is enhanced to improve the energy efficiency of the process without the negative effect of high butadiene content in the purified VCM.

Furthermore, another objective of the present invention was to provide an improved process for the production of vinyl chloride by thermal cracking of 1,2-dichloroethane, in which the EDC conversion in the cracking unit is enhanced to increase the VCM production capacity without the negative effect of high butadiene content in the purified VCM.

The inventors found that these objectives were achieved by a process for the production of vinyl chloride by thermal cracking of 1,2-dichloroethane (EDC) to form a reaction mixture containing vinyl chloride (VCM), hydrogen chloride (HCl), unconverted 1,2-dichloroethane, the impurity 1,3-butadiene and other by-products in which said mixture is quenched and said vinyl chloride is separated from said mixture, and where said 1,3-butadiene is removed from said quenched mixture prior to said vinyl chloride separation by reacting with chlorine added to said mixture after addition of a butadiene reduction agent to said mixture.

Said butadiene reduction agent is selected from the classes of compounds known to or expected to act as radical scavengers.

Said butadiene reduction agent is an aromatic compound selected from the groups consisting of aromatics with one or more oxygen attached to the ring.

Preferably, said butadiene reduction agent is a para-substituted phenol as 4-methoxyphenol, 4-cresol or hydroquinone.

The present invention will be further explained and elucidated in connection with the following examples and the attached figure.

Fig. 1 shows a simplified process scheme for EDC cracking to VCM.

The present invention involves a modification in the process, i.e. in the process stream after the quench column 2 and prior to the VCM column 4, preferably in the bottom of the HCl-column 3 or between the HCl column 3 and the VCM column 4, with typical process temperature in the range 60-120°C where chlorine and a butadiene reduction agent are added to said process stream

Since the EDC conversion typically exceeds 50%, the process stream is dominated by the product VCM. VCM is an unsaturated hydrocarbon and therefore reactive towards chlorine even at moderate temperatures, whereas the component that is desired to react with chlorine, 1,3-butadiene, only is present in the stream in a concentration below 100 ppm. The reaction conditions are thus challenging with respect to selectivity; the objective is to react the trace component, butadiene, and not the dominating component, VCM. As will be documented, the selectivity towards butadiene is highly dependent on temperature and VCM concentration. At low temperature (20-50°C) and low concentration of VCM in the EDC stream (< 1%), the selectivity towards chlorination of butadiene is very high and almost 100% conversion of butadiene can be achieved. However, an increase in the VCM/EDC–ratio to a value corresponding to 55% EDC conversion and a raise in the temperature above 50°C has a strong negative influence on the selectivity towards butadiene chlorination. The added chlorine will preferably react with VCM into trichloroethane (TCE) instead of reacting with butadiene.

The inventors have, however, surprisingly found that by first adding an agent in ppm levels to the process stream, followed by chlorine addition, butadiene reduction is enhanced dramatically at temperatures above 50°C. Without being limited to any particular explanation, the inventors suggest that the agent functions as a radical scavenger that limits the reaction of VCM with chlorine into TCE and enhances the reaction between chlorine and butadiene.

The general mechanism of the reaction between a radical scavenger (R-H) and a chlorine radical can be written as

$$R\text{-}H + Cl^* \rightarrow R^* + HCl$$

The radical chain reaction is retarded by reacting the chlorine radical to HCl and creating a stable radical R*. Molecules with radical scavenger properties are typically those that can create radicals stabilised by resonance upon H abstraction, such as phenols.

From general knowledge in chemistry, it is rather surprising that a radical reaction mechanism should be significant at such low temperatures in the absence of radiation or initiators, since the bond dissociation energy of the Cl_2 molecule is as high as 240 kJ/mole, making the concentration of chlorine radicals extremely low at these temperatures. Addition of Cl_2 to an olefin like VCM, is therefore assumed to proceed via a polar mechanism, whereas formation of TCE by substitution on EDC would require temperatures around 300°C, according to the literature (J. D. Roberts and M. C. Caserio, “Basic Principles of Organic Chemistry”, W. A. Benjamin Inc. 1981). Furthermore, in a recent SRI Consulting report (2000) from the Process Economics Program (“Process Econimics Program Report 5D, Vinyl Chloride”, March 2000, Process Economics Program, SRI Consulting, Menlo Park California, 94025), the liquid phase high temperature chlorination (HTC) of ethylene is claimed to proceed by an electrophilic ionic mechanism at temperatures around 84-160°C. This reaction is quite analogous to the chlorination of VCM to TCE, except that VCM is less reactive than ethylene. However, the observed effect of adding an agent with radical scavenging properties, supports this understanding of the chemistry. At low temperature, the chlorination reaction proceeds via an electrophilic ionic (hereafter polar) mechanism, which favours the selective reaction of butadiene into dichlorobutenes. At higher reaction temperatures, chlorination by a radical mechanism becomes increasingly important. Chlorination by this mechanism has a very low selectivity, and VCM chlorination to TCE is the major reaction due to the high VCM concentration. By adding a small amount of a butadiene reduction agent (typically 1-600 ppm by weight relative to EDC) with properties as described above the additive serves as a radical scavenger that reduces the rate of VCM chlorination and enhances the selectivity for butadiene chlorination. Although structurally similar to the catalysts disclosed in US 3624169, there are definite differences:

As is to be expected for this class of radical scavengers, meta-substituted phenols are less active than the para-substituted ones, whereas meta-substituted phenols are the preferred ones in US 3624169. It is familiar to those skilled in the art that the density of the unpaired electron in the corresponding radical (after H abstraction) will be distributed among the ortho- and para positions and that substituents in these positions will tend to stabilise the radical, whereas meta substituents have negligible stabilisation effects in comparison with the ortho- and para substituents. In US 3624169, on the other hand, the meta-substituted phenols m-cresol (3-methylphenol) and resorcinol (1,3-dihydroxybenzene) are the most active ones and para substituted phenols are excluded altogether. In the present invention, the use of ortho substituted phenols seems to be considerably less favourable compared to para substituted ones. This is rather surprising in light of the explanation given above, but may perhaps be due to more steric hindrance around the hydroxyl group in the case of ortho substituents, causing the kinetics of H abstraction to be too slow to give any retardation effect on the radical chain reaction.

Furthermore, the catalyst disclosed in US 3624169 is claimed to be stable and not consumed during the reaction. The butadiene reduction agent used in the present invention is consumed by reaction with radicals in the solution as shown above and will lose its effect upon repeated additions of chlorine.

Hence, the behaviour and effect of the catalyst disclosed in US 3624169 and the butadiene reduction agent used in the present invention are entirely different.

In an EDC/VCM stream representing 55% EDC conversion and with butadiene level as low as 15 ppmmol, a butadiene conversion of 60% can be achieved by adding 30 ppm by weight 4-methoxyphenol relative to EDC and 400 ppmmol chlorine relative to the total stream. The formation of TCE is less than 200 ppmmol relative to the total stream. These results are achieved with EDC from the bottom of the VCM column 4 in Fig. 1 of a VCM plant, which contains all the typical chlorinated by-products, including chloroprene (1600 ppmmol).

In the case of higher cracker conversion, more butadiene will be formed, requiring a higher butadiene conversion to get on-spec VCM. The butadiene conversion can be increased by increasing the amount of chlorine and butadiene reduction agent. An undesired effect would be increased formation of TCE, but the accepted amount of TCE will also increase with increasing EDC conversion, because of the improved energy efficiency of the cracking process.

The butadiene reduction agent should be selected from the classes of compounds known to act or expected to be able to act as radical scavengers, preferably para-substituted phenols and most preferably 4-methoxyphenol.

Examples

The chlorination of 1,3-butadiene was typically performed in an autoclave (1liter, Autoclave Engineers) especially designed and constructed for utilisation in reactions involving chlorine. The autoclave was equipped with stirring, thermocouples and pressure transmitters for exact monitoring of the process conditions.

Unless otherwise stated, the following reagents and procedure were used:

1. 1,2-dichlorethane (EDC), p.a. purity from Merck
2. EDC delivered from a VCM production plant, sampled from the bottom of the VCM column 4. The EDC contains the typical range of heavy by-products formed in EDC cracking. The content of chloroprene was 1600 ppmmol and the content of trichloroethane (TCE) was 40 ppmmol.
3. Vinyl chloride (VCM) delivered from a PVC plant. The quality is identical to the one used for industrial scale polymerisation.
4. 1,3-butadiene (> 98%)

5. Chlorine (99% Cl_2). Chlorine was mixed with EDC (p.a.) corresponding to a solution of 2 wt % chlorine in EDC.

The autoclave was filled with EDC (300 g) at ambient conditions. The butadiene reduction agent was dissolved or blended into EDC before filling to the autoclave. Butadiene in an amount corresponding to 15-1000 ppmmol of the total autoclave content was introduced from a syringe to EDC in the autoclave with a small amount of continuous N_2 purge gas and with stirring. Finally VCM (240 g) was added to the autoclave with stirring and the autoclave was heated to the desired temperature, resulting in a pressure around 13 bar at 100°C and conditions corresponding to 55% cracker conversion. When the desired reaction conditions were established, a solution of 2 wt % Cl_2 in p.a. EDC (8 g) was added to the autoclave.

The reaction was monitored by withdrawal of liquid samples from the autoclave (250 μl) through a sample loop and into evacuated ampoules (2 litre). The vaporised sample was analysed for VCM, butadiene, chloroprene, TCE, 1,4-dichlorobutene, cis- and trans-3,4-dichlorobutene by a GC (Gas Cromatograph) equipped with a FID (Flame Ionisation Detector) detector. The reaction was typically completed within 1 hour reaction time.

Example 1: Reactivity of butadiene, chloroprene and VCM

The reactivity of butadiene, chloroprene and VCM towards chlorination was investigated in experiments in the autoclave as well as in a dark glass flask heated in a water bath. Experiments in a glass flask were performed with 200-240 g EDC (plant quality) containing 1600 ppmmol chloroprene to which was added 1000 ppmmol VCM and 15 ppmmol butadiene at ambient conditions. After heating to reaction temperature chlorine was added. Samples were withdrawn from the flask with a syringe and analysed on a GC. The experiments in the autoclave were performed with a synthetic mixture of VCM and EDC in a ratio corresponding to 55% EDC conversion using both p.a. EDC and EDC of plant quality. In the experiment with p.a. EDC, chloroprene was synthesised by dehydrochlorination of 3,4-dichloro-1-butene according to the procedure given in GB 119753, stabilised in

EDC and added to the autoclave, together with butadiene. The results are presented in Table 1.

Table 1. Conversion of butadiene, chloroprene and VCM in EDC (plant quality). Results from experiments in a glass flask or in the autoclave after complete reaction of chlorine.

Batch no	T °C	VCM at start ppmmol	Butadiene at start ppmmol	Chloroprene at start ppmmol	Cl_2 added ppmmol	VCM conv %	Butadiene conv %	Chloroprene conv %
23[1]	50	0	0	1600	1200	-	-	80
25[1]	60	1000	15	1600	350	10	94	20
20[2]	50	55 mol%	20	600[2]	300	0[3]	0	0
56	50	55 mol%	30	700	1300[4]	0[3]	70	15
55	100	55 mol%	30	700	1300[4]	0[3]	50	50

[1] Experiments in a glass flask
[2] Chloroprene synthesized according to GB 119753
[3] No measurable conversion
[4] 10g of a 6wt% Cl_2 in EDC solution was added

The results show that in EDC containing low levels of VCM, and at a moderate temperature, the reactivity of the by-products is as expected. Almost all butadiene is reacted with chlorine before chloroprene and then VCM is attacked. However, keeping the chlorine addition at 300 ppm and increasing the VCM concentration to a VCM/EDC ratio representing 55% conversion of EDC, the chlorination of butadiene and chloroprene does not take place (batch 20, in Table 1). The level of TCE in that experiment increased to 300 ppmmol, verifying that chlorine is reacted with VCM. By increasing the chlorine level further to 1300 ppm, one is able to achieve 70% conversion of butadiene at 50°C (batch 56), but raising the temperature to 100°C results in a loss in butadiene conversion to 50% (batch 55). In the latter two experiments, the formation of TCE was 900 and 1000 ppmmol, respectively. This signifies that almost all the added chlorine reacts with VCM into TCE, and results in a loss in VCM production and increased TCE formation. The latter two experiments were performed with the same butadiene/chloroprene ratio and chlorine/chloroprene ratio as given in US 3920761. The present results document that with a feed composition representative of the process stream after the HCl column, the removal of butadiene by chlorination at a temperature above 50°C is not feasible without losing a significant amount of the VCM produced. Thus, increasing EDC conversion above 55% would result in more butadiene formation, and would require more Cl_2 to achieve the required butadiene conversion, with more formation of TCE as a result.

Example 2: Effect of reaction temperature

The effect of the reaction temperature on butadiene chlorination was investigated with p.a. quality EDC, a VCM/EDC ratio corresponding to 55% EDC conversion, 20-700 ppmmol butadiene and typically stoichiometric amount of chlorine added. The results are shown in Table 2.

Table 2. Chlorination in the autoclave with 300 g EDC (p.a. quality), 240 g VCM and various amounts of butadiene and chlorine added. Results after complete reaction of chlorine.

Batch no	T °C	P bara	Stirring rpm	Butadiene at start ppmmol	Cl_2 added ppmmol	Butadiene conv. %	Dichloro-butenes ppmmol	TCE ppm-mol
11	20	2.6	100	400	400	60	150	15
17[1]	30	4.0	100	20	90	80	9	10
12	50	5.4	100	400	400	70	150	190
16	60	6.8	100	400	400	50	115	90
14	65	7.4	100	700	700	30	60	500
16	75	8.9	100	200	200	10	n.a.[3]	120
13	100	12.5	100	400	400	20	40	320
29[2]	100	14.2	1200	400	400	20	n.a.[3]	120

[1] EDC with 600 ppmmol chloroprene
[2] EDC of plant quality
[3] not analysed

Table 2 verifies that the conversion of butadiene is reduced with increasing temperature, as chlorine instead reacts with VCM into TCE. Treatment of a process stream representing 55% EDC conversion with chlorine after the HCl column at 100°C with a stoichiometric amount of chlorine will only result in about 20% conversion of butadiene. In a realistic process stream, the Cl_2/butadiene–ratio might be higher. As documented in Table 1 (batch 55), a chlorine/butadiene ratio of 43 results in 50% butadiene conversion. Table 2 also documents that at 30°C the butadiene conversion can be increased from around 60 to around 80% by adjusting the Cl_2/butadiene ratio from 1 to 4.

Example 3: Effect of butadiene reduction agent

The inventors assume that the reduction in butadiene conversion with increasing temperature is caused by a shift from a polar to a radical reaction mechanism. The dominance of the radical reaction mechanism can be reduced by adding a butadiene reduction agent, and the more selective, polar mechanisms thereby take over. Hence, it is possible to react butadiene which is present at trace levels, without attacking VCM to a significant extent. In the present invention and in contrast to what is disclosed in US 3624169 the ortho- and meta-substituted phenols have lower selectivity to butadiene chlorination than the para-substituted phenols which are preferred used in the present invention. All phenols give roughly the same amount of TCE (Table 3) in contrast to US 3624169, in which case 10-100 times more TCE is produced from para-phenols. The catalysts in US 3624169 are further claimed to be stable under reaction conditions, whereas the agent is consumed during the reaction in the present invention.

Furthermore, the loss of VCM as TCE is almost an order of magnitude lower than for the method disclosed in US 3920761. The current invention gives typically 150 ppm TCE at conditions corresponding to 55% cracker conversion, whereas the method disclosed in US 3920761 gives 1000 ppm TCE (Example 1).

Various compounds have been selected and tested for their function as butadiene reduction agents. The agent was mixed with EDC prior to filling in the autoclave. Table 3 lists the results with each additive.

Table 3. Chlorination with butadiene reduction agent in the autoclave with 300 g EDC (plant quality), 240 g VCM, 15 ppmmol chlorine added, 100°C, 16 bara, 1200 rpm. Results after various reaction time(t).

Batch no	Hydrocarbon added Type	mg	Butadiene conversion (%) t=5min	t=10 min	t=60min	Final TCE ppmmol
30[1]	None	-	17	17	20	600
28	Hydrochinone	30	n.a.[3]	n.a.[3]	50[2]	110
33[4]	Hydrochinone	40	15	30	50	100
51	2-methoxyphenol	55	10	20	20	200
52	3-methoxyphenol	55	20	30	30	100
34	4-methoxyphenol	40	50	60	90	130
54	2-cresol	40	0	0	0	200
39	3-cresol	30	20	25	25	150
53	4-cresol	55	40	60	60	150
42	Aniline	70	20	20	50	40
43	2,4,6-trimethylaniline	100	0	0	0	40
47	trans-1-phenyl-1-propene	60	15	20	20	180
48	Phenothiazine	40	30	40	40	80

[1] 400 ppmmol butadiene
[2] Analysis after 90 min
[3] not analysed
[4] 276 g VCM

Table 3 shows that several of the additives function as butadiene reduction agents: The conversion of butadiene is enhanced and the formation of TCE is reduced compared to the experiment without agent (batch 30). The most preferred hydrocarbon is 4-methoxyphenol (para-methoxyphenol) and 4-cresol (para-cresol). These additives were excluded as catalysts in US 3624169.

2-methoxyphenol and 3-cresol have almost no effect and can be considered inert as butadiene reduction agents, but these were found to be preferred catalysts in US 3624169.

2-cresol and trimethylaniline have the surprising effect of inhibiting the butadiene chlorination reaction almost completely; in the case of trimethylaniline there is also only a minor increase in TCE.

The additive denoted phenotioazine has two aromatic rings connected by two bridges; one with N and one with S. This compound functions as a butadiene reduction agent but is less preferred than the para-phenols.

Example 4: Effect of chlorine/butadiene-ratio and amount of agent added

The effect of varying the amount of 4-methoxyphenol and the amount of chlorine is documented in Table 4.

Table 4. Chlorination in the autoclave with 300 g EDC (plant quality), 240 g VCM and 15 ppmmol butadiene. Chlorination at 100°C, 16 bara, 1200 rpm. Various amounts of 4-methoxyphenol and chlorine added. Results after increasing reaction time (t).

Batch	Cl2 added	4-methoxyphenol	Butadiene conversion (%)			Final TCE
no	ppmmol	mg	t=5min	t=10 min	t=60min	ppmmol
34	400	40	50	60	90	130
35	400	200	45	60	60	70
36	400	10	50	60	60	100
37	100	30	0	0	0	10
38	700	43	60	70	80	300
44[1]	900	70	70	100	100	300
66	400	10	95	100	100	180
67	400	5	50	60	64	190

[1] 10 ppmmol butadiene in the feed

Table 4 shows that by adjusting the ratios of chlorine and butadiene reduction agent added, complete conversion of butadiene can be achieved even when the butadiene concentration in the feed is as low as 10 ppmmol (batch 44). The formation of TCE is still as low as 300 ppmmol and the surplus chlorine reacts with other by-products present in the EDC stream. In that experiment (batch 44) the butadiene conversion was 40% after only 1 min reaction time. This is important with respect to a process modification in a plant, as there might not be a need for a separate vessel added to the process.

Example 5: Butadiene removal from a feed reflecting enhanced EDC conversion

As discussed previously, there is a desire to increase the per-pass EDC conversion in the cracking tubes, in order to improve process economics. Increasing EDC conversion from 55 to 72% inherently increases the butadiene concentration in the product stream exiting the cracker. The function of a butadiene reduction agent in chlorination of butadiene in such a process stream was documented in experiments in the autoclave. The results are listed in Table 5.

Table 5. Chlorination in the autoclave with EDC (plant quality) and VCM corresponding to 65 and 72% EDC conversion and 500 ml total volume. Added 40-60 ppmmol butadiene and 4-methoxyphenol as radical scavenger.

Batch no	EDC conv. %	Butadiene added ppmmol	Cl2 added ppmmol	4-methoxy phenol mg	Butadiene conversion (%)			Final TCE ppmmol
					t=5min	t=10min	t=60min	
40	65	40	400	30	15	15	25	190
41	65	40	700	100	45	70	80	180
50	72	60	1100	155	70	75	80	500

The results demonstrate the function of the butadiene reduction agent in improving butadiene conversion without generation of excessive TCE, even at conditions representing 72% EDC conversion.

The positive effect of the butadiene reduction agent is maintained even in a process stream representing 72% EDC conversion. Thus, by the present invention the stream from the bottom of the HCl column towards the VCM column typically having a temperature of 60-120°C, can be treated with a butadiene reduction agent and chlorine, resulting in a significant reduction in the butadiene level in the purified VCM stream. The present invention makes it possible to increase the EDC conversion in the cracking unit without the negative effect of high butadiene content in the purified VCM. The invention improves the economics of the VCM production process by increasing the energy efficiency, and by reducing the cost of utilities per metric ton VCM produced. It also enables an increase in the plant production capacity.

Claims:

1. A process for the production of vinyl chloride by thermal cracking of 1,2-dichloroethane (EDC) to form a reaction mixture containing vinyl chloride (VCM), hydrogen chloride (HCl), unconverted 1,2-dichloroethane, the impurity 1,3-butadiene and other by-products in which said mixture is quenched and said vinyl chloride is separated from said mixture,

   characterised in that

   said 1,3-butadiene is removed from said quenched mixture prior to said vinyl chloride separation by reacting with chlorine added to said mixture after addition of a butadiene reduction agent to said mixture.

2. A process according to claim 1,

   characterised in that

   said butadiene reduction agent and said chlorine are added to said mixture after said quench but prior to said vinyl chloride separation.

3. A process according to claim 1,

   characterised in that

   said butadiene reduction agent and said chlorine are added to said mixture in the bottom of the HCl-column or between the HCl-column and the VCM-column in a plant for EDC cracking to VCM.

4. A process according to claim 1,

   characterised in that

   said reaction with said butadiene reduction agent and said chlorine is carried out at a temperature from 50 to 130°C.

5. A process according to claim 1,

   characterised in that

   said butadiene reduction agent is added in an amount of 1-600 ppmmol relative to EDC in said mixture.

6. A process according to claim 1,
characterised in that
said chlorine is added in an amount of 300-2000 ppmmol with respect to the amount of EDC and VCM in said mixture.

7. A process according to claim 1,
characterised in that
said butadiene reduction agent is selected from the classes of compounds known to or expected to act as radical scavengers.

8. A process according to claim 7,
characterised in that
said butadiene reduction agent is an aromatic compound selected from the groups consisting of aromatics with one or more oxygen attached to the ring.

9. A process according to claim 8,
characterised in that
said butadiene reduction agent is a para-substituted phenol.

10. A process according to claim 9,
characterised in that
said butadiene reduction agent is 4-methoxyphenol.

11. A process according to claim 9,
characterised in that
said butadiene reduction agent is 4-cresol.

12. A process according to claim 9,
characterised in that
said butadiene reduction agent is hydroquinone.

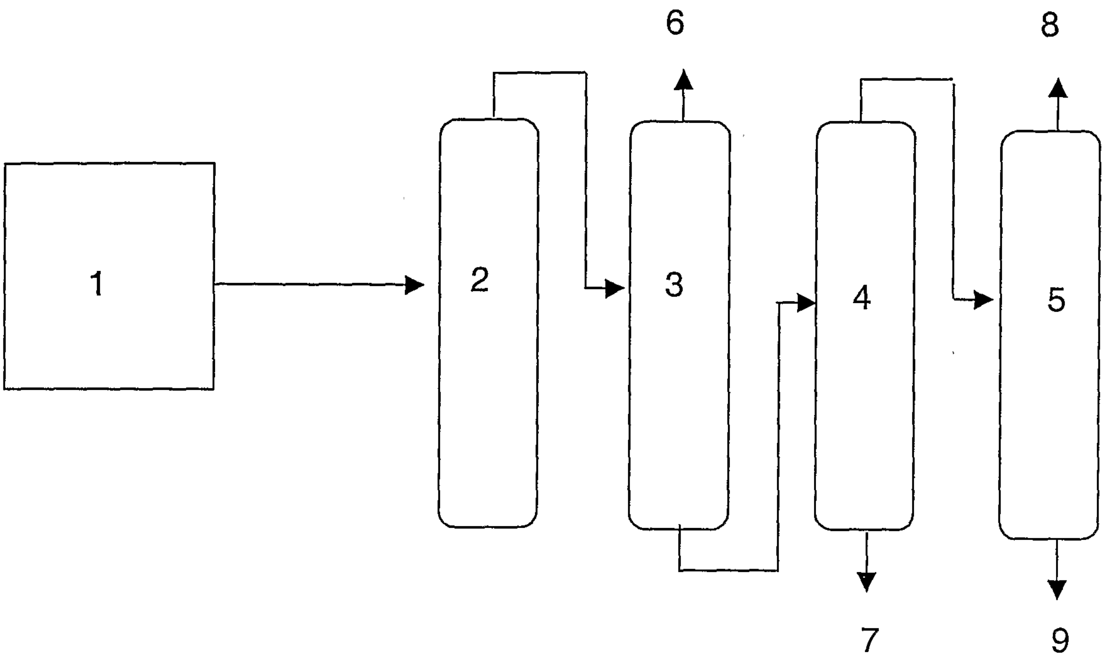

Fig. 1. A simplified process scheme for EDC cracking to VCM

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 2004/000284

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C07C 21/06, C07C 17/395, C07C 39/04, C07C 39/07, C07C 39/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ, CAS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3920761 A (GERD KROME), 18 November 1975 (18.11.1975), abstract; column 1, lines 54-57 --	1-8
Y	US 3624169 A (OTTO FRUHWIRTH), 30 November 1971 (30.11.1971), abstract; column 1, lines 70-74; example 5 --	1-8
A	US 4188347 A (LUDWIG SCHMIDHAMMER ET AL.), 12 February 1980 (12.02.1980), claims --	1-8
A	US 4225520 A (JOSEF RIEDL ET AL), 30 Sept 1980 (30.09.1980), claims -- --------	1-3

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

30/01/2005

International application No.
PCT/NO 2004/000284

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