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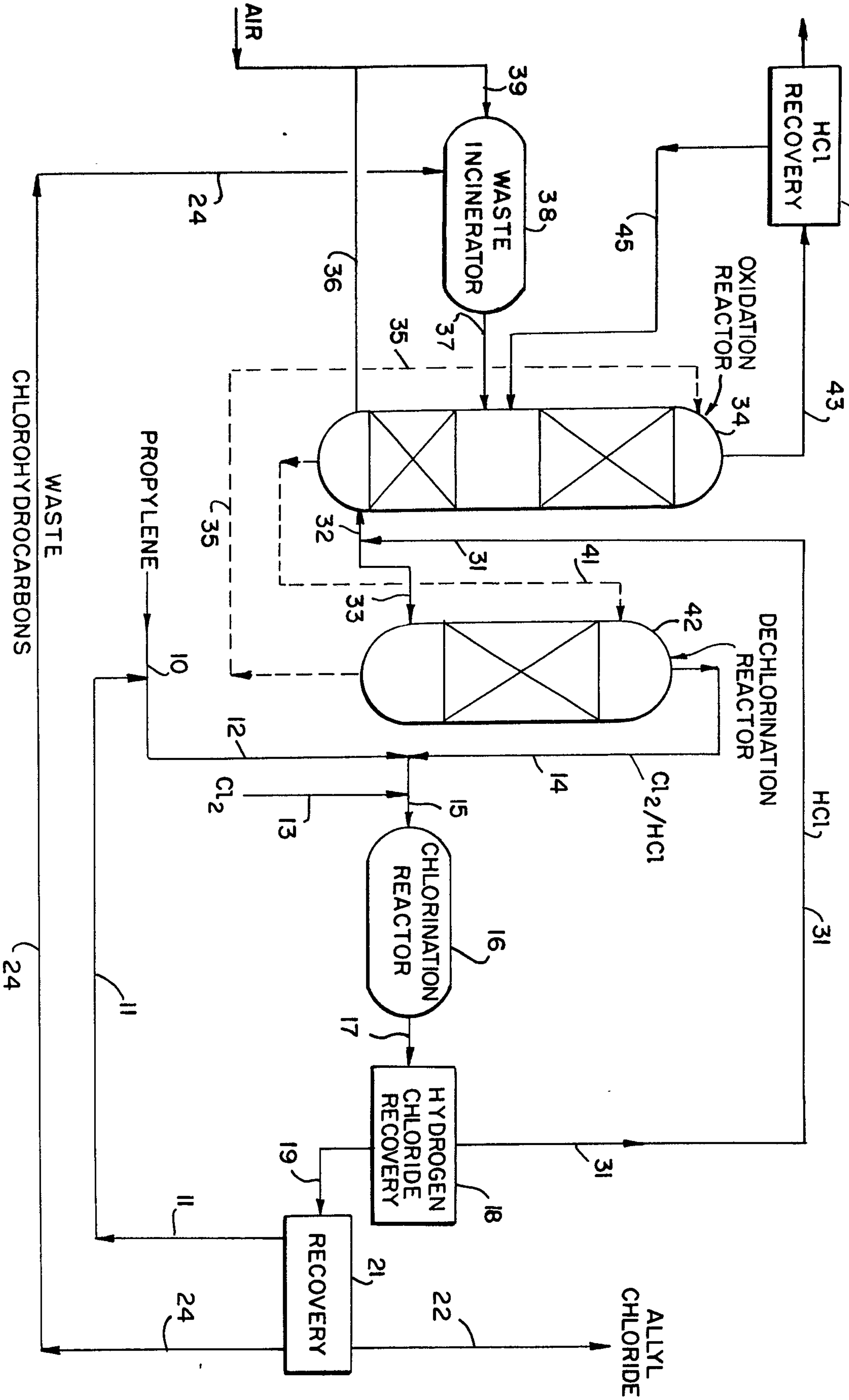
(54) Improvements in or relating to the production of allyl chloride

(57) Propylene is chlorinated with chlorine to produce allyl chloride and hydrogen chloride byproduct. Recovered hydrogen chloride byproduct is contacted with oxygen and a molten salt mixture containing higher and lower valent chlorides of a multivalent metal, such as copper, to recover the chlorine values of the hydrogen chloride by enriching the higher valent chloride content of the molten salt. The molten salt, enriched in higher valent chloride, is then dechlorinated by use of a stripping gas, preferably hydrogen chloride, to produce a gaseous effluent containing a mixture of stripped chlorine and the stripping gas which is then recycled to the chlorination step.


AIR
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WASTE INCINERATOR
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HCl RECOVERY
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OXIDATION REACTOR
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DECHLORINATION REACTOR
WASTE CHLOROHYDROCARBONS
PROPYLENE
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Cl2/HCl
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CHLORINATION REACTOR
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HYDROGEN CHLORIDE RECOVERY
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RECOVERY
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ALLYL CHLORIDE

SPECIFICATION

Improvements in or relating to the production of allyl chloride.

This invention relates to the production of allyl chloride and more particularly to the production of allyl chloride by the use of molten salts.

Molten salt mixtures, containing the higher and lower valent chlorides of a multivalent metal have been previously employed for the production of chlorinated hydrocarbons. Thus, for example, U.S.A. Patent Specification No. 3,879,482 describes a process for producing vinyl chloride wherein ethane and/or ethylene is contacted with a molten salt mixture containing the higher and lower valent chlorides of a multivalent metal, such as cuprous and cupric chloride, and hydrogen chloride and/or chlorine to produce an effluent containing vinyl chloride.

Similarly, U.S.A. Patent Specification No. 3,865,886 describes a process for the production of allyl chloride employing a molten salt mixture containing the higher and lower valent chlorides of a multivalent metal. In this process, propane is contacted with hydrogen chloride and/or chlorine and the molten salt mixture to produce an effluent containing allyl chloride.

The present invention relates to the production of chlorinated compounds by the use of molten salts, without direct contact between the fresh feed and the molten salt.

According to the present invention, there is provided a process for producing allyl chloride, comprising contacting in a chlorination zone propylene with chlorine to produce an effluent containing allyl chloride and hydrogen chloride, recovering allyl chloride and hydrogen chloride, introducing at least a portion of the recovered hydrogen chloride into an oxidation reaction zone wherein the hydrogen chloride is contacted with a molten salt mixture containing the higher and lower valent chlorides of a multivalent metal and oxygen to recover chlorine values by enriching the higher valent metal chloride content of the molten salt, passing molten salt from the oxidation reaction zone to a dechlorination zone wherein the molten salt is contacted with a stripping gas to strip chlorine from the molten salt, recovering gaseous chlorine from the dechlorination zone, and passing recovered gaseous chlorine as a recycle feed to the chlorination zone.

Preferably, the gaseous chlorine is recovered from the dechlorination zone mixed with stripping gas and the mixture is introduced into the chlorination zone.

Conveniently, the gaseous chlorine and stripping gas mixture is substantially free of water.

Suitably, the stripping gas employed in the dechlorination zone is a portion of the hydrogen chloride recovered from the effluent from the chlorination zone.

Advantageously, the gaseous chlorine and stripping gas mixture contains from 5 to 40 mole percent chlorine, and the molten salt mixture contains a mixture of cuprous and cupric chloride.

Usefully, the oxidation reaction zone is operated at a pressure of from 101 to 2027 kN/m^2 (1 to 20 atm) and a molten salt inlet temperature of from 398°C to 510°C (750°F to 950°F) and the dechlorination zone is operated at a pressure of from 10 to 304 kN/m^2 (0.1 to 3.0 atm), and a molten salt inlet temperature of from 454°C to 538°C (850°F to 1000°F).

Preferably, the oxidation reaction zone pressure is at least 50 kN/m^2 (0.5 atm) greater than the dechlorination zone pressure and the molten salt inlet temperature to the oxidation reaction zone is at least 28°C (50°F) less than the molten salt inlet temperature to the dechlorination zone.

Conveniently, the molten salt introduced into the dechlorination zone is free of water and of the oxide of the multivalent metal.

The molten salts employed in the present invention include the higher and lower valent forms of a chloride of a multivalent metal; i.e. a metal having more than one positive valent state, such as manganese, iron, copper, cobalt and chromium, preferably copper. In the case of higher melting multivalent metal chlorides, such as copper chlorides, a metal salt melting point depressant, which is non-volatile and resistent to the action of oxygen at the processing conditions, such as a chloride of a univalent metal; i.e., a metal having only one positive valent state, is added to the multivalent metal chloride to form a molten salt mixture having a reduced melting point. The metal chlorides employed as melting point depressants are preferably alkali metal chlorides, such as potassium and lithium chloride, in particular, but it is to be understood that other metal chlorides and mixtures thereof, such as the heavy metal chlorides; i.e. heavier than copper, of groups I,II and III and IV of the Periodic Table; e.g., zinc, silver and thallium chloride, may also be employed. the metal chloride melting point depressant is added in an amount sufficient to maintain the salt mixture as a melt at the reaction temperatures, and is generally added in an amount sufficient to adjust the melting point of the molten salt mixture to a temperature of below about 343°C (650°F). In the case of the salt mixture of copper chlorides and potassium chloride, the composition of the melt generally ranges from about 15% to about 40%, preferably about 20% to 25%, by weight, potassium chloride with the remainder being copper chlorides. It is to be understood, however, that in some cases the molten salt mixture may have a melting point higher than 343°C (650°F) provided that the mixture remains in the form of the melt throughout the processing steps. It is further to be understood that the melt may contain a mixture of multivalent metal chlorides or other reaction promotors.

As hereinabove indicated, hydrogen chloride by-product produced during the chlorination reaction is converted to chlorine for recycle to the chlorination step by the use of the molten salt, with such conversion being effected in two reaction zones. In particular, the hydrogen chloride byproduct is contacted with gaseous oxygen and the molten salt containing the higher and lower valent chlorides of the multivalent metal in an oxidation reaction zone to recover the chlorine values of the hydrogen chloride by enriching the higher valent metal chloride content of the molten salt.

The gaseous oxygen may be supplied as oxygen alone, or with another gas, preferably air, and is supplied in an amount sufficient to oxidise the hydrogen chloride and hence to enrich the higher valent chloride content of the salt. The precise amount of oxygen required for this conversion can be readily determined by those skilled in the art from the teachings herein. The amount of oxygen supplied is preferably chosen so that the molten salt withdrawn from the oxidation reaction zone is free of oxychloride. The oxidation reaction is represented by the following equations:

(1) $2CuCl + 1/2\ O_2 \qquad CuCl_2.\ CuO$
(2) $CuCl_2.\ CuO + 2\ HCl \qquad 2\ CuCl_2 + H_2O$
(3) $2\ CuCl + 1/2\ O_2 + 2HCl \qquad 2\ CuCl_2 + H_2O$

The molten salt mixture from the oxidation reaction zone, which is now enriched in the higher valent metal chloride is then introduced into the dechlorination reaction zone where chlorine is stripped from the salt, employing a stripping gas to facilitate such chlorine stripping. The amount of stripping gas employed is determined by the amount of chlorine desired in the dechlorination reactor effluent. The chlorine vapour pressure is determined by the temperature and the cupric chloride concentration, and for such a chlorine vapour pressure the total pressure is selected to provide the desired chlorine mole fraction.The moles of stripping gas per mole of chlorine is then:

$$\frac{\text{Total Pressure less Chlorine Partial Pressure}}{\text{Chlorine Partial Pressure}}$$

The conditions of the dechlorination and the amount of stripping gas provided are generally coordinated to provide a dechlorination effluent containing from 5 to 40 mole percent of chlorine.

The stripping gas employed for stripping chlorine from the molten salt is one which is inert with respect to the molten salt, and which is also preferably inert with respect to the subsequent chlorination reaction because in accordance with a preferred embodiment, chlorine produced in the dechlorination zone is not separated from the stripping gas before recycling to the chlorination operation. Examples of suitable stripping gases are hydrogen chloride, nitrogen, helium, and carbon dioxide. The preferred stripping gas is hydrogen chloride because hydrogen chloride is readily available in the process. The stripping of chlorine from the molten salt, employing copper chlorides as representative multivalent metal chlorides, is represented by the following equation:

(4) $2\ CuCl_2 \qquad 2\ CuCl + Cl_2$

The change in conditions mentioned above between the temperature and pressure of the oxidation reaction zone and those of the dechlorination reaction zone increases chlorine yields based on hydrogen chloride introduced into the oxidation reaction zone. The temperature change and change in the higher valent chloride concentration between the oxidation and dechlorination reaction zones can be achieved, without the use of heat exchange apparatus, by controlling the salt circulation rate. In general, the salt circulation rate is in the order of from about 20 to about 300 moles salt/mole Cl_2 stripped and preferably from about 40 to about 90 moles salt/mole Cl_2 stripped.

As mentioned above, the dechlorination reaction zone is maintained dry in order to avoid the presence of aqueous hydrogen chloride in the dechlorination effluent, and hence the necessity to separate large amounts of water from the chlorination effluent. The dechlorination reaction zone may be maintained in a dry state by introducing a dry stripping gas, and by preventing water from being present in the molten salt withdrawn from the oxidation reaction zone. The molten salt withdrawn from the oxidation reaction zone may be maintained in a dry state by contacting the salt, immediately prior to withdrawal thereof from the oxidation reaction zone, with hydrogen chloride feed to strip water therefrom. The hydrogen chloride also converts any copper oxide present in the salt so that the salt introduced into the dechlorination zone is free of both water and copper oxide.

The chlorine containing effluent withdrawn from the dechlorination reactor is usually recycled without further treatment to the chlorination zone but in some cases any entrained and vaporised salt is separated. The direct use of the dechlorination effluent, without separating the chlorine and the stripping gas has been found to result in a saving in heat and processing equipment costs. In addition, the stripping gas present in the chlorine functions as a diluent in the chlorination reaction which aids in stabilising and controlling the chlorination reaction temperature. It is also possible, however, to treat the dechlorination effluent to separate the stripping gas from the chlorine, so that chlorine, substantially in the absence of stripping gas, is recycled to the chlorination reaction. It is also possible to compress the recycle stream and/or heat or cool it, as appropriate, before feeding to the chlorination zone. The use of the stripping gas as a diluent for the chlorination is preferred because it affords good temperature control and thus improves the yield and increases the onstream time.

The propylene can be chlorinated to allyl chloride by procedures known in the art. In general, propylene is contacted with gaseous chlorine at a temperature of.from 316°C (600°F) to 598°C (1100°F) and preferably at 482°C (900°F) to 510°C (950°F). The chlorination is generally effected at a pressure of from 100 kN/m^2 (1 atm) to 500 kN/m^2 (5 atm). The chlorination does not require a catalyst, however, as should be apparent, a catalyst could be employed.

The chlorination reaction effluent generally contains, in addition to allyl chloride and hydrogen chloride, unreacted propylene, 1, 2-dichloropropane, and mono- and dichloropropylene. The unreacted propylene can be recovered and recycled to the chlorination reaction zone. Chlorinated reaction intermediates which are potentially convertible to allyl chloride, in particular 1, 2-dichloropropane, may be introduced into a further reaction zone for conversation to allyl chloride. In general, however, the quantity of 1, 2-dichloropropane produced does not warrant such further conversion and the chlorinated by-products, after separation from the other effluent components, are burnt. The combustion exhaust gases are then fed into the oxidation reactor for the recovery of their chlorine values.

In order that the invention may be more readily understood and so that further features thereof may be appreciated, the invention will now be described by way of example with reference to the accompanying drawing, which is a simplified schematic flow diagram of a process for the production of allyl chloride.

Propylene to be chlorinated, in line 10, is combined with recycle unreacted feed organic compound in line 11 and the combined stream in line 12 is combined with fresh feed chlorine in line 13 and a dechlorination reaction zone effluent in line 14, containing chlorine and hydrogen chloride, and obtained as hereinafter described. The combined stream in line 15 is introduced into a chlorination reactor, schematically generally indicated as 16.

In chlorination reactor 16, the propylene is chlorinated by direct contact with chlorine to produce allyl chloride, and hydrogen chloride byproduct, as well as other chlorinated C_3 compounds. The hydrogen chloride introduced with the feed does not react in the chlorination reactor.

A chlorination reaction zone effluent, containing allyl chloride, hydrogen chloride byproduct, unreacted feed and other byproducts, is withdrawn from reactor 16 through line 17 and introduced into a hydrogen chloride recovery zone, schematically indicated as 18, for recovering hydrogen chloride from the effluent. This zone 18 may, for example, comprise two columns (not shown) operated at two different pressures, with the gaseous effluent being introduced into the low pressure column, along with aqueous hydrogen chloride bottoms from the high pressure column, with the low pressure column being designed and operated to recover a gas stream substantially free of hydrogen chloride and an aqueous hydrogen chloride bottoms substantially free of organics. The bottoms recovered from the low pressure column is introduced into the high pressure column, which is designed and operated to recover substantially water free hydrogen chloride gas. The aqueous hydrogen chloride bottoms from the high pressure column (having a hydrogen chloride concentration lower than the liquid bottoms from the low pressure column) is then introduced into the low pressure column.

An organic product substantially free of hydrogen chloride and now containing water in line 19 is introduced into a separation and recovering section schematically generally indicated as 21 in order to effect drying thereof and recovery of reaction product, organic byproducts and recycle for the chlorination reactor. Thus, allyl chloride is recovered through line 22, and unreacted propylene feed is recovered through line 11 for recycle to the chlorination reactor 16.

Chlorinated hydrocarbon byproducts are recovered through line 24 for treatment as hereinafter described.

The hydrogen chloride recovered from zone 18 in line 31 is split into two portions, one portion of which, in line 32, is the net hydrogen chloride produced in the chlorination reactor 16 and the other portion, in line 33, being the portion employed as stripping gas for the dechlorination reactor. The net hydrogen chloride in line 32 is introduced into an oxidation reactor, schematically indicated as 34 for effecting recovery of the chlorine values.

The oxidation reactor 34 is provided through line 35 with a molten salt mixture, containing the higher and lower valent chlorides of a multivalent metal such as copper (i.e. cuprous chloride and cupric chloride) and a melting point depressant, such as potassium chloride, and is further provided with an oxygen containing gas, such as air, through line 36.

A chlorinated hydrocarbon combustion effluent, containing hydrogen chloride and some chlorine, is also introduced into reactor 34 through line 37. Such an effluent is obtained by burning the chlorinated byproducts in line 24 in a combustion zone 38 which is provided with air through line 39.

As a result of the contact between the hydrogen chloride, air and molten salt, the chlorine values of the hydrogen chloride are recovered by enriching the cupric chloride content of the molten salt. In addition, any gaseous chlorine present in the effluent in line 37 also enriches the cupric chloride content of the molten salt.

A gaseous effluent is withdrawn from reactor 34 through line 43, and may include equilibrium amounts of hydrogen chloride, and chlorine, if any, as well as components introduced with the combustion effluent in line 37, such as carbon oxides, and with the air, such as nitrogen. The effluent in line 43 is further treated in a hydrogen chloride recovery zone 44, as known in the art, in order to recover aqueous hydrogen chloride in line 45 which is recycled to the oxidation reactor 34. Such a treatment is described in U.S.A. Patent Specification No. 3,963,200.

A molten salt, now enriched in cupric chloride, is withdrawn from reactor 34 through line 41 and introduced into the top of a dechlorination reactor, schematically generally indicated as 42. The dechlorination reactor is provided with hydrogen chloride stripping gas through line 33, and as a result of the conditions in reactor 42 and the stripping action of the hydrogen chloride, gaseous chlorine is stripped from the salt, with the cupric chloride being converted to cuprous chloride.

Molten salt withdrawn from reactor 42 is recycled to reactor 34 through line 35.

A dechlorination effluent, containing gaseous chlorine and the hydrogen chloride which was introduced as stripping gas, is withdrawn from reactor 42 through line 14, for introduction into the chlorination reactor 16. The chlorine stripped from the salt is that produced from the hydrogen chloride generated in reactor 16, as well as any chlorine values recovered from waste chlorinated product produced in the chlorination reactor 16 and burnt in the waste incinerator 38.

The mixture of chlorine and hydrogen chloride stripping gas is directly employed for the chlorination reaction; however, the effluent from the dechlorination reactor 42 may be treated to separately recover the chlorine for introduction into the chlorination reactor 16.

In addition, although the addition of hydrogen chloride as the stripping gas is preferred, the stripping of chlorine from the molten salt may be effected by the use of a stripping gas other than hydrogen chloride; e.g. nitrogen.

It is also to be understood that all or a portion of the byproducts recovered in line 24 could be separately recovered as product and/or recycle for further production of allyl chloride.

The invention will be further described, by way of example, with respect to the following example:

Example

The following provides in tabular form a flow scheme for producing allyl chloride in accordance with embodiment of the drawing. Flow rates are in moles per hour. The organics produced in reactor 16 are primarily various chlorinated C_3 hydrocarbons.

TABLE 1

	10	11	13	14	17	33	32	22	24
N_2			0.7	4.5	5.2	4.5	0.7		
O_2			0.2						
H_2O				0.4	0.6				
Cl_2			83.5	139.4					
CO_2			0.5	4.1	4.7	4.1	0.6		
H_2			0.3						
C_3H_6	200.5	466.8		0.7	467.8	1.0	0.2		
C_3H_5Cl					165.2			163.4	1.8
Organics		1.5			36.28			1.45	33.33
HCl		4.7		1487.4	1713.8	1487.4	221.7		
(Pressure psia	20	20	20	20	18	25	80	50	85)
kN/m^2	138	138	138	138	124	172	552	345	586
(Temp°F	80	110	80	905	950	80	80	100	200)
Temp°C	27	43	27	485	510	27	27	37	93

TABLE I cont.

	39	36	37	43	35	41	45	
N_2	1264	229	1264	1493.7				
O_2	334	60	197.4	185.2				
H_2O	55	11	116.6	495.0			224.1	
Cl_2			0.3	3.6				
CO_2			107.1	108.3				
HCl			58.1	23.7			29.2	
KCl					2407	2407		
CuCl					2661	2382		
$CuCl_2$					2956	3235		
(Pressure psia	85	80	80	80	75	75	21	80)
kN/m^2	586	552	552	517	517	145	552	
(Temp °F	80	80	-	770	775	910	310)	
Temp °C	27	27	-	410	413	488	154	

It has been found that the above described process permits allyl chloride production with effective recovery of hydrogen chloride by product for use in such production. In addition, it has been found that the use of recovered chlorine diluted with the stripping gas facilitates temperature control, which improves selectivity. In addition, in the described process chlorine does not have to be precisely metered to the chlorinator to avoid chlorinolysis and the resultant production of carbon, tars and byproducts. Thus, a more stable operation is achieved. Furthermore, the sensible heat of the dechlorination effluent in the described process can be recovered in the chlorinator.

CLAIMS

1. A process for producing allyl chloride, comprising contacting in a chlorination zone propylene with chlorine to produce an effluent containing allyl chloride and hydrogen chloride, recovering allyl chloride and hydrogen chloride, introducing at least a portion of the recovered hydrogen chloride into an oxidation reaction zone wherein the hydrogen chloride is contacted with a molten salt mixture containing the higher and lower valent chlorides of a multivalent metal and oxygen to recover chlorine values by enriching the higher valent metal chloride content of the molten salt, passing molten salt from the oxidation reaction zone to a dechlorination zone wherein the molten salt is contacted with a stripping gas to strip chlorine from the molten salt, recovering gaseous chlorine from the dechlorination zone, and passing recovered gaseous chlorine as a recycle feed to the chlorination zone.

2. A process according to claim 1, wherein the gaseous chlorine is recovered from the dechlorination zone mixed with stripping gas and the mixture is introduced into the chlorination zone.

3. A process according to claim 2, wherein the gaseous chlorine and stripping gas mixture is substantially free of water.

4. A process according to any one of the preceding claims, wherein the stripping gas employed in the dechlorination zone is a portion of the hydrogen chloride recovered from the effluent from the chlorination zone.

5. A process according to any one of claims 2 to 4, wherein the gaseous chlorine and stripping gas mixture contains from 5 to 40 mole percent chlorine.

6. A process according to any one of the preceding claims, wherein the molten salt mixture contains a mixture of cuprous and cupric chloride.

7. A process according to any one of the preceding claims, wherein the oxidation reaction zone is operated at a pressure of from 101 to 2027 kN/m^2 and a molten salt inlet temperature of from 398°C to 510°C and the dechlorination zone is operated at a pressure of from 10 to 304 kN/m^2, and a molten salt inlet temperature of from 454°C to 538°C.

8. A process according to any one of the preceding claims, wherein the oxidation reaction zone pressure is at least 50 kN/m^2 greater than the dechlorination zone pressure and the molten salt inlet temperature to the oxidation reaction zone is at least 28°C less than the molten salt inlet temperature to the dechlorination zone.

9. A process according to any one of the preceding claims, wherein the molten salt introduced into the dechlorination zone is free of water and of the oxide of the multivalent metal.

10. A process according to any one of the preceding claims, wherein the chlorination zone is operated at a temperature of from 316°C to 593°C.

11. A process according to any one of the preceding claims, wherein the chlorine recycle feed to the chlorination zone is supplemented by fresh feed chlorine.

12. A process substantially as herein described with reference to the accompanying drawing.

13. A process substantially as herein described with reference to the Example.

14. An allyl chloride whenever made by a process according to any one of the preceding claims.

15. An allyl chloride whenever made by a process substantially as herein described with reference to the accompanying drawing.

16. An allyl chloride whenever made by a process substantially as herein described with reference to the Example.

17. Any novel feature or combination of features herein described.

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