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(54) Title: PROCESS FOR THE PRODUCTION OF ETHYLENE, HYDROGEN CHLORIDE, AND VINYL CHLORIDE FROM ETHANE

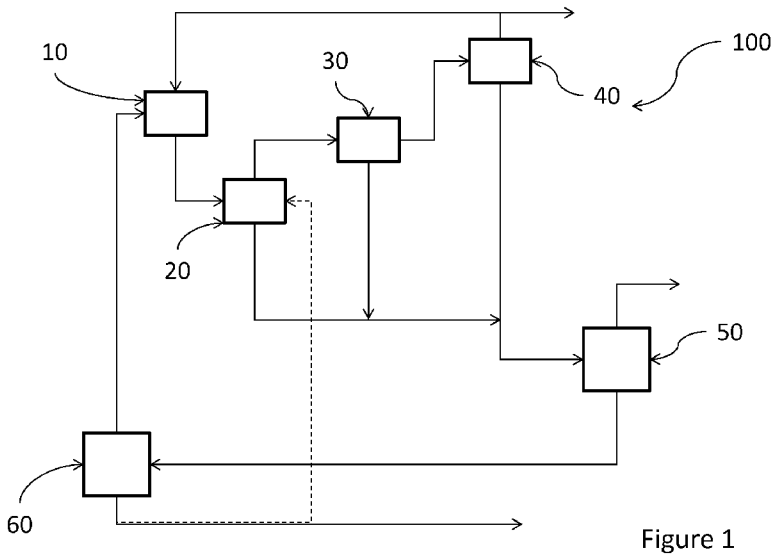


Figure 1

(57) Abstract: A process is provided for the chlorination of ethane using chlorine as the chlorinating agent to produce primarily vinyl chloride (VCM), ethylene, hydrogen chloride (HCl).

PROCESS FOR THE PRODUCTION OF ETHYLENE, HYDROGEN CHLORIDE, AND VINYL CHLORIDE FROM ETHANE

The present invention relates to a method of producing vinyl chloride (VCM), ethylene and hydrogen chloride (HCl) by chlorinating ethane using chlorine (Cl_2) as the chlorinating agent. The invention further relates to the recycle to extinction of ethyl chloride and the partial recycling of ethane, ethylene, and hydrogen chloride (HCl) byproduct to produce zero net production of ethylene.

The foregoing products have traditionally been prepared from more expensive sources of hydrocarbons. Dating back to the early part of this century, the large scale production of vinyl chloride, trichloroethylene and perchloroethylene commenced with the use of acetylene however acetylene is a relatively expensive raw material. When the ethylene oxychlorination process was developed during the 1950's, acetylene was supplanted by less costly ethylene as a feedstock for chlorinated hydrocarbons. Up to the present time practically all chlorinated ethane/ethylene products have been derived from ethylene.

Although ethylene is produced in large quantities by world-scale plants, its cost is necessarily higher than the price of ethane from which it is preferentially made. Contributing to ethylene's cost is the necessity of employing complex, high-temperature cracking processes with inherent inefficiencies. Therefore, there would be a significant advantage of substituting ethane for ethylene in the manufacture of chlorinated ethane/ethylene. Particularly in the case of the manufacture of vinyl chloride, which requires about 0.45 pounds of ethylene per pound of product, any savings in the cost of hydrocarbon raw material would be important.

In order to circumvent the shortcomings of existing technology, numerous attempts have been made to chlorinate ethane by cost-effective means. One such method, for example, that employs various chlorinating agents including C_2Cl_6 combined with hydrogen chloride and chlorine is described in U.S. Pat. No. 5,097,083. While U.S. Pat. No. 5,097,083 demonstrated the use of C_2Cl_6 as a chlorinating agent, in some cases C_2Cl_6 may be unfavorable because additional operating and capital costs are needed to produce the chlorinating agent C_2Cl_6. For example, an oxychlorination reactor was proposed to chlorinate the C_2Cl_4 precursor for C_2Cl_6 and additional separation columns were needed to purify and recycle C_2Cl_4 and HCl. Another method, disclosed in U.S. Pat. No. 2,628,259, teaches chlorination of ethane to co-produce VCM

and vinylidene chloride (1,1-dichloroethylene) uses a high chlorine to ethane molar ratio which in turn, corresponds to low selectivity of the desired VCM and ethylene products. In contrast, CA2097434 teaches a process of high selectivity ethylene by chlorination ethane but at a lower than 1.1 molar ratio of chlorine to ethane that makes the process yield lower than 50% to the desired product.

It is therefore an object of the present invention to provide a continuous process for producing vinyl chloride, hydrogen chloride, ethylene and heavies comprising:

a) reacting a feed comprising chlorine with ethane in a reaction zone to produce a crude product wherein the crude product comprises
   i. a partial recycle fraction comprising HCl and ethylene,
   ii. an extinction recycle fraction comprising ethyl chloride, and
   iii. product components;
b) fractionally separating from the crude product the partial recycle fraction;
c) fractionally separating the extinction recycle fraction from the remaining crude product; and
d) fractionally separating product components into a heavies stream and remaining product components.

As used herein "adiabatic" means: the chlorination process or reaction occurs without transfer of heat between the reactor and its surroundings. The process is said to be nearly adiabatic because the reactor is insulated or designed in such a manner that heat is not intentionally added or removed from the reactor.

As used herein "exit temperature" means: the temperature of reactor effluent. The chlorine to ethane feed ratio is one of the variables used to control the exit temperature. This chlorine:ethane molar ratio ranges from 1.1 to 3.0, alternatively from 1.5 mol. to 2.5 mol. The exit temperature ranges from 350 – 700 °C, alternatively from 375 – 675 °C, further alternatively from 400 – 650 °C.

As used herein "inlet temperature" means: the mixed temperature of all component of the feed components stream as they enter the reactor wherein the feed components comprise ethane chlorine partial recycle fraction, and recycle to extinction fraction. The inlet temperature ranges from 200°C - 350°C, alternatively from 250 – 330 °C, further alternatively from 260 – 320 °C.

As used herein "partial recycle fraction" means: primarily hydrogen chloride and ethylene. The components of the partial recycle fraction are products of the present invention and are fractionally separated from the crude product.

As used herein "extinction recycle fraction" means: ethyl chloride. The extinction recycle fraction is fractionally separated from the crude product in the present invention

As used herein "product components" means: primarily vinyl chloride (VCM), ethylene, heavies, and HCl. HCl, Vinyl chloride (VCM) and heavies are products of the present invention.

As used herein "heavies" means: primarily 1,2-dichloroethane, 1,1-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, Vinylidene chloride (1,1-dichloroethylene)

The components of the product components are fractionally separated from the crude product. The components of the heavies are products of the present invention.

As used herein "recycle to extinction" means: one or more components of the recycle stream that is recycled at the same mass rate as produced and thus at steady state. This recycled component(s) is not removed as a product from the process. In the process of the present invention, the extinction recycle fraction is recycled to extinction.

All endpoint range values provided herein are inclusive and combinable. All percentages are percentages by weight. "Primarily" is intended to mean greater than 80% by weight, alternatively greater than 85% by weight, further alternatively greater than 90% by weight.

FIG. 1 is a schematic view of the operation of a preferred embodiment of the process of the invention. Referring to the Figure, the process of the present invention is carried out as follows.

A feed containing components of ethane and chlorine is fed to a reactor ("reaction zone"). Optionally, the feed components may also comprise ethylene, ethane and chlorine. The feed components are preheated either individually or in combination in any manner and at any time prior to entry into the reactor 10. Prior art reference, CA 2097434 premixes ethane and chlorine below 200°C and heats the mixture after adding it to the reactor. This method requires heat exchangers and thus is more capital intensive than the process of the present invention which uses a reactor 10 that is nearly adiabatic. Chlorine may be preheated to the inlet temperature or alternatively may comprise a temperature ranging from 20° to 80°C before it is combined with the ethane and/or the extinction and/or partial recycle fraction. The chlorine may

be co-fed into the reactor 10 with the ethane, mixed with the ethane and then added to the reactor 10, or added by other conventional means of introducing materials into a reactor.

Conventional reactors may be used. One suitable example of a reactor is a jet-stirred reactor. The temperature of the reactor 10 at the time of entry of feed ("inlet temperature") ranges from 200 – 350 °C, alternatively from 250 – 330 °C, further alternatively from 260 – 320 °C. The thermal chlorination reaction is carried out in the reactor 10. The chlorine is highly reactive with the ethane and reacts to produce a crude product comprising a partial recycle fraction, an extinction recycle fraction, product components, and heavies.

With the near adiabatic reactor condition, the exothermic reaction increases the crude product to temperature higher than 350°C up to 700°C to produce a vapor reaction product components. This vapor crude product is cooled to produce vapor phase and liquid reactor effluent. Suitable cooling methods include heat exchanging with coolant or by adjusting feed ratios.

The vapor phase and liquid reactor effluent are cooled further in a condenser 20 to condense the liquid. The liquid is provided preferably to a distillation column 40, or alternatively to a separation column 50. The vapor phase is compressed at a pressure greater than or equal to 689 kPa, alternatively greater than or equal to 1378 kPa and further alternatively greater than or equal to 1930 kPa by compressor 30 for efficient separation of ethylene and HCl from VCM in the distillation column 40. The partial recycle fraction is fractionally separated from the crude product and a portion of the partial recycle fraction can be optionally returned to the reaction zone such that the ethylene has no net production rate in the overall process.

The distillation column 40 bottom stream is fed to the separation column 50 where VCM is stripped of heavies. Limits on distillation column 40 bottom temperature should be less than or equal to 150°C, alternatively less than or equal to 100°C to minimize fouling/polymerization. The overhead stream of VCM can be purified to very high levels for sale or significant amounts of HCl can be allowed to slip out the bottom of distillation column 40 and be sent for further purification to an existing or new conventional VCM finishing plant. Separation column 50 is operated such that less than 100ppm of HCl is in overheads of separation column 50. More HCl impurity could be included if the process is integrated with a conventional VCM plant with excess VCM finishing capacity.

The bottom stream of separation column 50 comprising extinction recycle fraction and heavies is fractionally separated and fed to column 60 where the extinction recycle fraction is recovered in the overhead stream and optionally partially recycled or completely recycled to extinction to the reactor 10. The overheads of column 60 can also be sold or further separated as an ethyl chloride product. The column 60 bottom stream comprising heavies is fractionally separated and sent to column 20 as a liquid quench media of the reactor outlet or can be optionally partially recycled to reactor 10. The rest of the heavies can be further processed to remove dichloroethane products for use as feed in a downstream EDC thermal cracking process to produce VCM. Alternatively the remaining heavies can also be used as feed to produce trichloroethylene and/or perchloroethylene. The process of the present invention is continuous.

The products produced by the present invention are valuable items of commerce. For example, VCM is consumed in huge quantities in the manufacture of plastic materials. These product components can be directly fed to VCM cracking production unit where the dichloroethanes can be further cracked to VCM. In this way, the raw material cost to produce dichloroethanes and VCM can be reduced by replacing ethylene with ethane. HCl and ethylene can be further fed to an oxychlorination reactor to produce 1,2-dichloroethane.

The reaction of the present invention is highly efficient as greater than 95%; alternatively greater than 99% of the chlorine is converted during the reaction. The reaction of the present invention is highly efficient as greater than 80%; alternatively greater than 85% of the ethane is converted during the reaction.

EXAMPLE

Process for the Chlorination of Ethane

Ethane is chlorinated to produce ethylene, HCl, vinylidene, and VCM in a thermal chlorination jet-stirred reactor. The jet-stirred reactor was simulated as described in Chapter 8.7 in "Cleaner Combustion: Developing Detailed Kinetics Models," F. Battin-Leclerc, J.M. Simmie, E. Blurock (Ed) (2013)) using kinetics reported by Dahl et al. [Ind. Eng. Chem. Res. 2001, 40, 2226-2235]. The thermodynamic properties were obtained from reported literature values (see http://webbook.nist.gov/chemistry/) and thermochemical kinetics approach (see S.W. Benson "Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters," 1976). The reactor model was imbedded inside a process flow sheet

simulation (see http://www.aspentech.com/products/aspen-plus.aspx) such that impacts of recycle were evaluated.

The reactor has pressure of 40psia and the feed is preheated to higher than 200°C. The reactor exit temperature is maintained by adjusting chlorine flow rate. The residence time is about 0.5 sec to 1 second depending on whether outlet or inlet flow rate is used, respectively. The crude liquid product composition is given below in Table 1.

Table 1. Process Operating Conditions and Product Composition

Fresh Feed Ethylene/Ethane, (mass ratio)	4
Cl_2/Ethane (molar ratio)	1.8
Partial Recycle Fraction/Fresh Ethane, (mass ratio)	5
Extinction Recycle Fraction/Fresh Ethane, mass ratio	0.62
Reactor flow/reactor volume, kgmoles/hr/m^3	576
Inlet Temperature, °C	293
Outlet Temperature, °C	500
Chlorine Conversion	>99
Ethane Conversion	86%
Total Product Composition, wt%	
HCl	31.5
Ethane	1.5
Ethylene	42.8
Vinyl chloride	14.3
Heavies	9.9
Heavies composition, wt %	
1,2-dichloroethane	50.3
1,1-dichloroethane	29.8
1,1,1-trichloroethane	16.0
1,1,2-trichloroethane	1.8
Vinylidene chloride (1,1-dichloroethylene)	1.7
other	0.4
Partial recycle fraction Recycle, wt %	Wt%
HCl	41.5
Ethane	2.0
Ethylene	56.4
Other	0.1

CLAIMS:

We claim:

1. A continuous process for producing vinyl chloride, hydrogen chloride, ethylene and heavies comprising:
    a) reacting a feed comprising chlorine with ethane in a reaction zone to produce a crude product wherein the crude product comprises
        i. a partial recycle fraction comprising HCl and ethylene,
        ii. an extinction recycle fraction comprising ethyl chloride, and
        iii. product components;
    b) fractionally separating from the crude product the partial recycle fraction;
    c) fractionally separating the extinction recycle fraction from the remaining crude product; and
    d) fractionally separating product components into a heavies stream and remaining product components.
2. The process of claim 1 wherein at least a portion of the partial recycle fraction is recycled to the reaction zone.
3. The process of claim 1 wherein the extinction recycle fraction is returned to the reaction zone.
4. The process of claim 1 wherein the extinction recycle fraction is recycled to extinction.
5. The process of claim 1 wherein the chlorine:ethane molar ratio of the feed ranges from 1.1 to 3.0
6. The process of claim 1 wherein the reaction is conducted at near adiabatic condition.
7. The process of claim 1 wherein the inlet temperature ranges from 250 – 350 °C.
8. The process of claim 1 wherein the reactor comprises an exit temperature ranging from 350 – 700 °C.
9. The process of claim 1 wherein the feed stream components are pre-mixed prior to being fed in the reactor.
10. The process of claim 1 wherein the feed stream components are not pre-mixed prior to being fed in the reactor and mixed as they entered the reactor

11. The process of claim 1 further wherein greater than 95% of the chlorine is converted into products.
12. The process of claim 1 wherein greater than 80% of ethane is converted into products.
13. The process of claim 12 further wherein greater than 80% of ethane is converted into products.
14. The process of claim 1 wherein the feed further comprises ethylene.
15. The process of claim 1 wherein the heavy streams is partially recycled to quench reactor effluent.

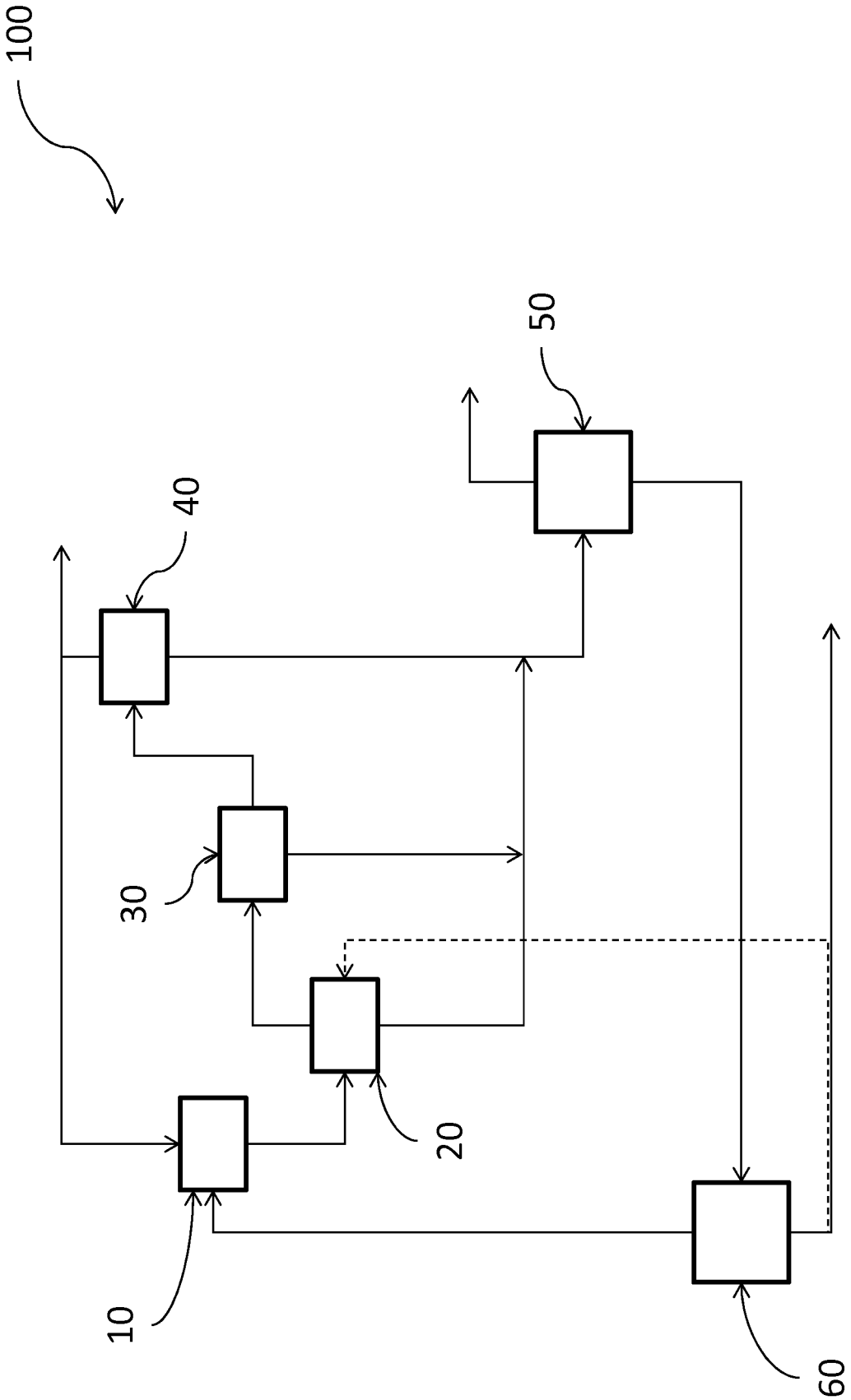


Figure 1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/053165

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C17/00 C07C17/10 C07C21/06
ADD.

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)
C07C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 143 850 A2 (LUMMUS CO) 9 February 1973 (1973-02-09)	1-5,7-15
Y	figures 1-3 page 11, line 35 - page 13, line 36 page 15 claims 1-17	6

X	FR 2 178 078 A1 (LUMMUS CO [US]) 9 November 1973 (1973-11-09)	1-5,7-15
Y	figures 1-2 page 11, line 21 - page 14, line 8 claims 1-9	6

X	FR 2 281 911 A1 (LUMMUS CO [US]) 12 March 1976 (1976-03-12)	1-5,7-15
Y	figures 1-2 page 6, line 33 - page 10, line 10 claims 1-13	6

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[X] Further documents are listed in the continuation of Box C.

[X] 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

"E" earlier application or patent but published on or after the international filing date

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 December 2015	11/12/2015

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/053165

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 705 728 A (VISWANATHAN KRISHNAN [US] ET AL) 6 January 1998 (1998-01-06)	1-5,7-15
Y	abstract figure 1 column 4, line 39 - column 7, line 24 column 9, lines 48-53 claims 1-22	6

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2015/053165

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