(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 April 2013 (11.04.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/052471 A1

(51) International Patent Classification:
C07C 67/317 (2006.01) *C07C 51/42* (2006.01)
C07C 69/54 (2006.01) *C07C 57/04* (2006.01)

(21) International Application Number:
PCT/US2012/058441

(22) International Filing Date:
2 October 2012 (02.10.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

13/251,623	3 October 2011 (03.10.2011)	US
13/424,779	20 March 2012 (20.03.2012)	US
13/632,248	1 October 2012 (01.10.2012)	US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2013/052471 A1

(54) Title: PROCESSES FOR PRODUCING ACRYLIC ACIDS AND ACRYLATES

(57) Abstract: In one embodiment, the invention is to a process for producing an acrylate product. The process comprises the step of providing a crude acrylate product comprising the acrylate product and an alkylenating agent. The process further comprises the steps of removing inert and/or reactive gases from the crude product to form a liquid acrylate stream, diluting the liquid acrylate stream with a diluent to form a diluted liquid acrylate stream, and then separating at least a portion of the diluted liquid acrylate stream to form an alkylenating agent stream and an intermediate product stream. The alkylenating agent stream comprises at least 1 wt.% alkylenating agent and the intermediate product stream comprises acrylate product.

PROCESSES FOR PRODUCING ACRYLIC ACIDS AND ACRYLATES

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. App. No. 13/632,248, filed on October 1, 2012, and also claims priority to U.S. App. No. 13/424,779, filed March 20, 2012, which claims priority to U.S. App. No. 13/251,623, filed on October 3, 2011, the entireties of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to the production of acrylate product. More specifically, the present invention relates to the production of crude acrylic acid via the condensation of acetic acid. The crude product may be diluted and separated to form a finished acrylic acid product.

BACKGROUND OF THE INVENTION

[0003] α,ß-unsaturated acids, particularly acrylic acid and methacrylic acid, and the ester derivatives thereof are useful organic compounds in the chemical industry. These acids and esters are known to readily polymerize or co-polymerize to form homopolymers or copolymers. Often the polymerized acids are useful in applications such as superabsorbents, dispersants, flocculants, and thickeners. The polymerized ester derivatives are used in coatings (including latex paints), textiles, adhesives, plastics, fibers, and synthetic resins.

[0004] Because acrylic acid and its esters have long been valued commercially, many methods of production have been developed. One exemplary acrylic acid ester production process utilizes: (1) the reaction of acetylene with water and carbon monoxide; and/or (2) the reaction of an alcohol and carbon monoxide, in the presence of an acid, e.g., hydrochloric acid, and nickel tetracarbonyl, to yield a crude product comprising the acrylate ester as well as hydrogen and nickel chloride. Another conventional process involves the reaction of ketene (often obtained by the pyrolysis of acetone or acetic acid) with formaldehyde, which yields a crude product comprising acrylic acid and either water (when acetic acid is used as a pyrolysis reactant) or

methane (when acetone is used as a pyrolysis reactant). These processes have become obsolete for economic, environmental, or other reasons.

[0005] More recent acrylic acid production processes have relied on the gas phase oxidation of propylene, via acrolein, to form acrylic acid. The reaction can be carried out in single- or two-step processes but the latter is favored because of higher yields. The oxidation of propylene produces acrolein, acrylic acid, acetaldehyde and carbon oxides. Acrylic acid from the primary oxidation can be recovered while the acrolein is fed to a second step to yield the crude acrylic acid product, which comprises acrylic acid, water, small amounts of acetic acid, as well as impurities such as furfural, acrolein, and propionic acid. Purification of the crude product may be carried out by azeotropic distillation. Although this process may show some improvement over earlier processes, this process suffers from production and/or separation inefficiencies. In addition, this oxidation reaction is highly exothermic and, as such, creates an explosion risk. As a result, more expensive reactor design and metallurgy are required. Also, the cost of propylene is often prohibitive.

[0006] The aldol condensation reaction of formaldehyde and acetic acid and/or carboxylic acid esters has been disclosed in literature. This reaction forms acrylic acid and is often conducted over a catalyst. For example, condensation catalysts consisting of mixed oxides of vanadium and phosphorus were investigated and described in M. Ai, *J. Catal.*, 107, 201 (1987); M. Ai, *J. Catal.*, 124, 293 (1990); M. Ai, *Appl. Catal.*, 36, 221 (1988); and M. Ai, *Shokubai*, 29, 522 (1987).

[0007] Processes for preparing acrylic acid from methanol and acetic acid or from ethanol and formaldehyde have been disclosed in U.S. Pat. Pubs. 2012/0071688 and 2012/0071687. In U.S. Pat. Pub. 2012/0071688, the process for preparing acrylic acid from methanol and acetic acid feeds at least one inert diluent gas other than steam to a reaction zone. This diluent may be air or may be fed to the reactor from the methanol oxidation process.

[0008] Even in view of these references, the need exists for processes for producing finished acrylate product that utilize improved diluent feed configurations without sacrificing conversion, selectivity and/or yield.

[0009] The references mentioned above are hereby incorporated by reference.

BRIEF DESCRIPTION OF DRAWINGS

[0010] The invention is described in detail below with reference to the appended drawings, wherein like numerals designate similar parts.

[0011] FIG. 1 is a process flowsheet showing an acrylic acid reaction/separation system in accordance with an embodiment of the present invention.

[0012] FIG. 2 is a schematic diagram of an acrylic acid reaction/separation system in accordance with one embodiment of the present invention.

[0013] FIG. 3 is a schematic diagram of an additional acrylic acid reaction/separation system in accordance with another embodiment of the present invention.

SUMMARY OF THE INVENTION

[0014] In a first embodiment, the present invention relates to a process for producing an acrylate product, the process comprising the steps of reacting in a reactor a reaction mixture comprising alkanoic acid and an alkylenating agent to form a crude acrylate product; removing inert and/or reactive gases from the crude acrylate product to form a liquid acrylate stream; diluting the liquid acrylate stream with a diluent to form a diluted liquid acrylate stream; and separating at least a portion of the diluted liquid acrylate stream to form a finished acrylate product. Alkanoic acid conversion may be at least 30% and alkylenating agent conversion may be at least 50 %. The diluent may be selected from the group consisting of water, an alkanoic acid, acrylic acid, and combinations thereof. In some embodiments, the diluent is acetic acid. In other embodiments, the diluent is a combination of acetic acid and water. The diluted liquid acrylate stream may comprise acrylate product and alkanoic acid, wherein the ratio of acrylate product to alkanoic acid is less than 0.25:1. The diluted liquid acrylate stream may comprise from 30 wt% to 90 wt% alkanoic acid, less than 50 wt% acrylate product, and less than 15 wt.% alkylenating agent. In some embodiments, the separating step may utilize a separation unit other than a liquid-liquid extraction column. The separating may further comprise separating at least a portion of the diluted liquid acrylate stream to form an alkylenating agent stream comprising at least 1 wt% alkylenating agent and an intermediate acrylate product stream comprising acrylate product and alkanoic acid. The separating may further comprise separating the intermediate acrylate product to form the finished acrylate product comprising acrylate product and a finished alkanoic acid stream comprising alkanoic acid; and directing at least a portion of the finished

alkanoic acid stream to the crude acrylate product. The finished alkanoic acid stream may comprise less than 10 wt.% acrylate product.

[0015] In a second embodiment, the present invention is directed to a process for producing an acrylate product, the process comprising the steps of providing a crude acrylate product comprising acrylate product, alkanoic acid and alkylenating agent; removing inert and/or reactive gases from the crude acrylate product to form a liquid acrylate stream; diluting the crude acrylate product with alkanoic acid to form a diluted liquid acrylate stream comprising from 30 wt.% to 90 wt.% alkanoic acid, and separating at least a portion of the diluted liquid acrylate stream to recover a finished acrylate product.

[0016] In a third embodiment, the present invention is directed to a process for producing an acrylate product, the process comprising the steps of reacting in a reactor a reaction mixture comprising acetic acid and formaldehyde to form a crude acrylate product; removing inert and/or reactive gases from the crude acrylate product to form a liquid acrylate stream; diluting the crude acrylate product with additional acetic acid to form a diluted liquid acrylate stream, and separating at least a portion of the diluted liquid acrylate stream to recover a finished acrylate product. The separating may comprise separating acetic acid from the diluted liquid acrylate stream and recycling the separated acetic acid to the reactor. The relative volatility of the alkylenating agent to acetic acid, after dilution, may be at least 1:1. The diluted liquid acrylate stream may comprise from 30 to 75 wt.% alkanoic acid.

[0017] In a fourth embodiment, the present invention is directed to a process for increasing alkylenating agent volatility, the process comprising the steps of reacting in a reactor a reaction mixture comprising alkanoic acid and an alkylenating agent to form a crude acrylate product; removing inert and/or reactive gases from the crude acrylate product to form a liquid acrylate stream; diluting the crude acrylate product with an alkanoic acid to form a diluted liquid acrylate stream; and separating at least a portion of the diluted liquid acrylate stream to form an alkylenating agent stream comprising at least 10 wt.% alkylenating agent and a finished acrylate product. The amount of alkylenating agent in the alkylenating stream may be greater than the combined amount of alkylenating in other derivative streams. The liquid acrylate stream may be further diluted with additional water.

[0018] In a fifth embodiment, the present invention is directed to a process for producing an acrylate product, the process comprising the steps of reacting in a reactor a reaction mixture

comprising alkanoic acid and an alkylenating agent to form a diluted crude acrylate product; separating at least a portion of the diluted crude acrylate product to form a finished acrylate product; wherein conversion of the alkanoic acid is less than 30%.

DETAILED DESCRIPTION OF THE INVENTION

Introduction

[0019] Production of unsaturated carboxylic acids such as acrylic acid and methacrylic acid and the ester derivatives thereof via most conventional processes have been limited by economic and environmental constraints. In the interest of finding a new reaction path, the aldol condensation reaction of acetic acid and an alkylenating agent, e.g., formaldehyde, has been investigated. This reaction may yield a unique crude product that comprises, *inter alia*, a higher amount of (residual) formaldehyde, which is generally known to add unpredictability and problems to separation schemes. Although the aldol condensation reaction of acetic acid and formaldehyde is known, there has been little if any disclosure relating to the effects of the dilution of a crude acrylate product stream and/or the derivatives thereof. It has now been discovered that the dilution may, surprisingly and unexpectedly, affect alkylenating agent volatility and acrylate product recovery.

[0020] In one embodiment, the present invention is to a process for producing an acrylate product. The process may comprise the step of reacting in a reactor a reaction mixture comprising an alkanoic acid, e.g., acetic acid, and an alkylenating agent to form a crude acrylate product. Inert and/or reactive gases, either from the reaction mixture or formed as by-products during the reaction, may be removed from the crude acrylate product to form a liquid acrylate stream.

[0021] In one embodiment, the inert and/or reactive gases are removed from the crude acrylate product and purged from the system via a purge stream. The purge stream preferably purges only a minimal amount of reactants and products (if any). In some embodiments, the purge stream comprises less than 5 wt.% acrylate product, e.g., less than 3 wt.% or less than 1 wt.%. In terms of ranges, the purge stream may comprise from 0.01 to 5 wt.% acrylate product, e.g., from 0.1 to 3 wt.% or from 0.1 to 1 wt.%. The purge stream may also comprise less than 10 wt.% alkanoic acid and alkylenating agent, combined, e.g., less than 7.5 wt.% or less than 5 wt.%. In

terms of ranges, the purge stream may comprise from 0.01 to 10 wt.% alkanoic acid and alkylenating agent combined, e.g., from 0.1 to 7.5 wt.% or from 0.1 to 5 wt.%.

[0022] Returning to the separation process, the liquid acrylate stream may then be diluted with a diluent to form a diluted liquid acrylate stream. It has now been found that the dilution of the liquid acrylate stream provides for unexpected improvements in separation efficiencies. Without being bound by theory, it is believed that the addition of diluent to the liquid acrylate stream increases the volatility of the alkylenating agent. This increase in volatility eases the separation of the alkylenating agent from the alkanoic acid and acrylate product, allowing for increased efficiencies in the recovery of reactant alkylenating agent and increased purity of the finished alkanoic acid stream and of the finished acrylate product. In some embodiments, the relative volatility of the alkylenating agent to acetic acid may be at least 1:1, e.g., at least 1.05:1, at least 1.1:1 or at least 1.15:1.

[0023] In one embodiment, the diluted liquid acrylate stream may be separated to form an alkylenating agent stream comprising at least 1 wt.% alkylenating agent, and an intermediate acrylate product stream comprising acrylate product and alkanoic acid. The intermediate acrylate product may then be separated to form the finished acrylate product comprising acrylate product and a finished alkanoic acid stream comprising alkanoic acid. The finished alkanoic acid stream may comprise less than 10 wt.% acrylate product, e.g., less than 7.5 wt.%, less than 5 wt.%, or less than 2.5 wt.% acrylate product. At least a portion of the finished alkanoic acid stream may be directed to the liquid acrylate stream or to the reactor. The separating step may utilize separation units other than liquid-liquid extraction column(s).

[0024] The diluent may be selected from the group consisting of water, an alkanoic acid, e.g., acetic acid, acrylic acid, and combinations thereof. In some embodiments, the diluent is acetic acid or a combination of acetic acid and water. As explained herein, at least a portion of the diluent may be supplied via the finished alkanoic acid stream, e.g., finished acetic acid stream. At least a portion of the finished alkanoic acid stream may be recycled and utilized as diluent. The liquid acrylate stream may then be diluted with additional acetic acid to form a diluted liquid acrylate stream. Additionally, acetic acid other than residual acetic acid that remains in the crude acrylate product, may be utilized to dilute the liquid acrylate stream. In one embodiment, acetic acid from an outside source may be utilized. In one embodiment, a separate acetic acid feed is utilized to dilute the liquid acrylate stream.

[0025] The diluted liquid acrylate stream may comprise from 30 to 90 wt.% diluent, e.g., from 40 to 90 wt.% or from 50 to 90 wt.%. In embodiments where the diluent is acetic acid, the diluted liquid acrylate stream may comprise from 30 to 90 wt.% acetic acid, e.g., from 40 to 90 wt.% or from 50 to 90 wt.%. It is understood that some of the acetic acid in the diluted liquid acrylate stream may be unreacted acetic acid from the reaction mixture. The amount of acetic acid in the diluted liquid acrylate stream may be controlled by increasing or decreasing acetic acid conversion. In some embodiments, acetic acid conversion is at least 30%, e.g., at least 40%, at least 50% or at least 60%.

[0026] In embodiments wherein both water and acetic acid are used to dilute the liquid acrylate stream, the diluted liquid acrylate stream may comprise form 30 to 90 wt.% acetic acid, e.g. from 40 to 90 wt.% acetic acid or from 50 to 90 wt.% acetic acid, and from 10 to 60 wt.% water, e.g., from 10 to 50 wt.% water or from 10 to 40 wt.% water. In one embodiment, the water and the acetic acid are added separately to the liquid acrylate stream. In one embodiment, the water and the acetic acid may be combined and then used to dilute the liquid acrylate stream.

[0027] The diluted liquid acrylate stream comprises acrylate product and alkanoic acid in a ratio of less than 0.25:1 acrylate product to alkanoic acid, e.g., less than 0.20:1, less than 0.15:1 or less than 0.10:1. The diluted liquid acrylate stream also comprises less than 50 wt.% acrylate product, e.g., less than 40 wt.% acrylate product or less than 30 wt.% acrylate product. In terms of ranges, the diluted liquid acrylate stream comprises from 0.1 to 50 wt.% acrylate product, e.g., from 0.5 to 40 wt.%, or from 1 to 30 wt.%. The diluted liquid acrylate stream further comprises less than 15 wt.% alkylenating agent, e.g., less than 10 wt.% alkylenating agent, less than 5 wt.% alkylenating agent, or less than 3 wt.% alkylenating agent. In terms of ranges, the diluted liquid acrylate stream may comprise from 0.1 to 15 wt.% alkylenating agent, from 0.1 to 5 wt.% alkylenating agent, or 0.1 to 3 wt.% alkylenating agent.

[0028] The alkylenating agent conversion may be at least 50%, e.g., at least 60%, or at least 70%.

[0029] In another embodiment, the inventive process comprises the steps of providing a crude acrylate product comprising acrylate product, alkanoic acid and alkylenating agent and removing inert and/or reactive gases from the crude acrylate product to form a liquid acrylate stream. The liquid acrylate stream may then be diluted with a diluent comprising alkanoic acid to form a diluted liquid acrylate stream comprising from 30 to 90 wt.% alkanoic acid. The

diluted liquid acrylate stream may then be separated to recover a finished acrylate product and a finished alkanoic acid stream. At least a portion of the finished alkanoic acid stream may be recycled to be used as diluent.

[0030] In one embodiment, the inventive process comprises the step of reacting in a reactor a reaction mixture comprising acetic acid and formaldehyde to form a crude acrylate product. Inert and/or reactive gases may be removed from the crude acrylate product to form a liquid acrylate stream. The liquid acrylate stream may then be diluted with additional acetic acid to form a diluted liquid acrylate stream. For example, acetic acid other than the residual acetic acid that remains in the crude acrylate product, may be utilized to dilute the liquid acrylate stream. In one embodiment, acetic acid from an outside source may be utilized. In one embodiment, a separate acetic acid feed is utilized to dilute the liquid acrylate stream. The diluted liquid acrylate stream may comprise from 30 to 90 wt.% acetic acid, e.g., from 40 to 90 wt.% or from 50 to 90 wt.%. At least a portion of the diluted liquid acrylate stream may be separated to recover a finished acrylate product. At least a portion of the diluted liquid acrylate stream may be separated to recover a finished acetic acid stream and at least a portion of the finished acetic acid stream may be recycled to the reactor. At least a portion of the finished acetic acid stream may also be used to dilute the liquid acrylate stream.

[0031] In another embodiment, the inventive process comprises the step of reacting in a reactor a reaction mixture comprising alkanoic acid and an alkylenating agent in a ratio of at least 1.5:1, e.g., at least 2:1, or at least 2.5:1, to form a diluted crude acrylate product. Conversion of acetic acid may be less than 30%, e.g., less than 25% or less than 20%. At least a portion of the diluted crude acrylate product may be separated to form a finished acrylate product. Without being bound by theory, it is believed that by controlling the conversion of acetic acid to be less than 30%, the diluted crude acrylate product has improved separation of alkylenating agent from the diluted crude acrylate product due to increased alkylenating agent volatility in the diluted crude acrylate product.

[0032] In one embodiment, the inventive process is directed to increasing alkylenating agent volatility. The process may comprise the step of reacting in a reactor a reaction mixture comprising alkanoic acid and an alkylenating agent to form a crude acrylate product. Inert and/or reactive gases may be removed from the crude acrylate product to form a liquid acrylate stream. The liquid acrylate stream may then be diluted with an alkanoic acid to form a diluted

liquid acrylate stream. Water may additionally be added as a diluent. At least a portion of the diluted liquid acrylate stream may be separated to form a finished acrylate product and an alkylenating agent stream comprising at least 10 wt.% alkylenating agent, e.g., at least 15 wt.% or at least 20 wt.% alkylenating agent. The amount of alkylenating agent in the alkylenating agent stream is greater than the combined amount of alkylenating agent in other derivative streams in the separation process. These other derivative streams include distillate and residue streams from each of the separation steps described herein.

[0033] As used herein, acrylic acid, methacrylic acid, and/or the salts and esters thereof, collectively or individually, may be referred to as "acrylate products." The use of the terms acrylic acid, methacrylic acid, or the salts and esters thereof, individually, does not exclude the other acrylate products, and the use of the term acrylate product does not require the presence of acrylic acid, methacrylic acid, and the salts and esters thereof.

[0034] The inventive process, in one embodiment, provides a diluted liquid acrylate stream comprising the acrylic acid and/or other acrylate products. The diluted liquid acrylate stream of the present invention, unlike most conventional acrylic acid-containing crude products, further comprises a significant portion of at least one alkylenating agent. Preferably, the at least one alkylenating agent is formaldehyde. For example, the diluted liquid acrylate stream may comprise at least 0.5 wt.% alkylenating agent(s), e.g., at least 1 wt.%, at least 5 wt.%, at least 7 wt.%, at least 10 wt.%, or at least 25 wt.%. In terms of ranges, the diluted liquid acrylate stream may comprise from 0.5 wt.% to 50 wt.% alkylenating agent(s), e.g., from 1 wt.% to 45 wt.%, from 1 wt.% to 25 wt.%, from 1 wt.% to 10 wt.%, or from 5 wt.% to 10 wt.%. In terms of upper limits, the diluted liquid acrylate stream may comprise less than 50 wt.% alkylenating agent(s), e.g., less than 45 wt.%, less than 25 wt.%, or less than 10 wt.%.

[0035] In one embodiment, the diluted liquid acrylate stream of the present invention further comprises water. For example, the diluted liquid acrylate stream may comprise less than 60 wt.% water, e.g., less than 50 wt.%, less than 40 wt.%, or less than 30 wt.%. In terms of ranges, the diluted liquid acrylate stream may comprise from 1 wt.% to 60 wt.% water, e.g., from 5 wt.% to 50 wt.%, from 10 wt.% to 40 wt.%, or from 15 wt.% to 40 wt.%. In terms of upper limits, the diluted liquid acrylate stream may comprise at least 1 wt.% water, e.g., at least 5 wt.%, at least 10 wt.%, or at least 15 wt.%.

[0036] The diluted liquid acrylate stream of the present invention comprises very little, if any, of the impurities found in most conventional acrylic acid products. For example, the diluted liquid acrylate stream of the present invention may comprise less than 1000 wppm of such impurities (either as individual components or collectively), e.g., less than 500 wppm, less than 100 wppm, less than 50 wppm, or less than 10 wppm. Exemplary impurities include acetylene, ketene, beta-propiolactone, higher alcohols, e.g., C_{2+}, C_{3+}, or C_{4+}, and combinations thereof. Importantly, the diluted liquid acrylate stream of the present invention comprises very little, if any, furfural and/or acrolein. In one embodiment, the diluted liquid acrylate stream comprises substantially no furfural and/or acrolein, e.g., no furfural and/or acrolein. In one embodiment, the diluted liquid acrylate stream comprises less than less than 500 wppm acrolein, e.g., less than 100 wppm, less than 50 wppm, or less than 10 wppm. In one embodiment, the diluted liquid acrylate stream comprises less than less than 500 wppm furfural, e.g., less than 100 wppm, less than 50 wppm, or less than 10 wppm. Furfural and acrolein are known to act as detrimental chain terminators in acrylic acid polymerization reactions. Also, furfural and/or acrolein are known to have adverse effects on the color of purified product and/or to subsequent polymerized products.

[0037] In addition to the acrylic acid and the alkylenating agent, the diluted liquid acrylate stream may further comprise acetic acid, water, propionic acid, and light ends such as oxygen, nitrogen, carbon monoxide, carbon dioxide, methanol, methyl acetate, methyl acrylate, acetaldehyde, hydrogen, and acetone. Exemplary compositional data for the liquid acrylate stream are shown in Table 1. Components other than those listed in Table 1 may also be present in the diluted liquid acrylate stream.

TABLE 1

DILUTED CRUDE ACRYLATE PRODUCT COMPOSITIONS

Component	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Acrylic Acid	1 to 75	1 to 50	5 to 50	10 to 40
Alkylenating Agent(s)	0.5 to 50	1 to 45	1 to 25	1 to 10
Acetic Acid	1 to 90	1 to 70	10 to 70	40 to 60
Water	1 to 60	5 to 50	5 to 40	10 to 50
Propionic Acid	0.01 to 10	0.1 to 10	0.1 to 5	0.1 to 1
Oxygen	0.01 to 10	0.1 to 10	0.1 to 5	0.1 to 1
Nitrogen	0.1 to 20	0.1 to 10	0.5 to 5	0.5 to 4
Carbon Monoxide	0.01 to 10	0.1 to 10	0.1 to 5	0.5 to 3
Carbon Dioxide	0.01 to 10	0.1 to 10	0.1 to 5	0.5 to 3
Other Light Ends	0.01 to 10	0.1 to 10	0.1 to 5	0.5 to 3

Production of Acrylate Products

[0038] Any suitable reaction and/or separation scheme may be employed to form the crude acrylate product as long as the reaction provides the diluted liquid acrylate stream components that are discussed above. For example, in some embodiments, the acrylate product stream is formed by contacting an alkanoic acid, e.g., acetic acid, or an ester thereof with an alkylenating agent, e.g., a methylenating agent, for example formaldehyde, under conditions effective to form the crude acrylate product stream. Preferably, the contacting is performed over a suitable catalyst. The crude acrylate product may be the reaction product of the alkanoic acid-alkylenating agent reaction. In a preferred embodiment, the crude acrylate product is the reaction product of the aldol condensation reaction of acetic acid and formaldehyde, which is conducted over a catalyst comprising vanadium and titanium. In one embodiment, the crude acrylate product is the product of a reaction in wherein methanol with acetic acid are combined to generate formaldehyde *in situ*. The aldol condensation then follows. In one embodiment, a methanol-formaldehyde solution is reacted with acetic acid to form the crude acrylate product.

[0039] The alkanoic acid, or an ester of the alkanoic acid, may be of the formula R'-CH_2-COOR, where R and R' are each, independently, hydrogen or a saturated or unsaturated alkyl or aryl group. As an example, R and R' may be a lower alkyl group containing for example 1-4 carbon atoms. In one embodiment, an alkanoic acid anhydride may be used as the source of the alkanoic acid. In one embodiment, the reaction is conducted in the presence of an alcohol,

preferably the alcohol that corresponds to the desired ester, e.g., methanol. In addition to reactions used in the production of acrylic acid, the inventive catalyst, in other embodiments, may be employed to catalyze other reactions.

[0040] The alkanoic acid, e.g., acetic acid, may be derived from any suitable source including natural gas, petroleum, coal, biomass, and so forth. As examples, acetic acid may be produced via methanol carbonylation, acetaldehyde oxidation, ethylene oxidation, oxidative fermentation, and anaerobic fermentation. As petroleum and natural gas prices fluctuate, becoming either more or less expensive, methods for producing acetic acid and intermediates such as methanol and carbon monoxide from alternate carbon sources have drawn increasing interest. In particular, when petroleum is relatively expensive compared to natural gas, it may become advantageous to produce acetic acid from synthesis gas ("syngas") that is derived from any available carbon source. US Patent No. 6,232,352, which is hereby incorporated by reference, for example, teaches a method of retrofitting a methanol plant for the manufacture of acetic acid. By retrofitting a methanol plant, the large capital costs associated with carbon monoxide generation for a new acetic acid plant are significantly reduced or largely eliminated. All or part of the syn gas is diverted from the methanol synthesis loop and supplied to a separator unit to recover carbon monoxide and hydrogen, which are then used to produce acetic acid.

[0041] In some embodiments, at least some of the raw materials for the above-described aldol condensation process may be derived partially or entirely from syngas. For example, the acetic acid may be formed from methanol and carbon monoxide, both of which may be derived from syngas. For example, the methanol may be formed by steam reforming syngas, and the carbon monoxide may be separated from syngas. In other embodiments, the methanol may be formed in a carbon monoxide unit, e.g., as described in EP2076480; EP1923380; EP2072490; EP1914219; EP1904426; EP2072487; EP2072492; EP2072486; EP2060553; EP1741692; EP1907344; EP2060555; EP2186787; EP2072488; and US Patent No. 7842844, which are hereby incorporated by reference. Of course, this listing of methanol sources is merely exemplary and is not meant to be limiting. In addition, the above-identified methanol sources, inter alia, may be used to form the formaldehyde, e.g., *in situ*, which, in turn may be reacted with the acetic acid to form the acrylic acid. The syngas, in turn, may be derived from variety of carbon sources. The carbon source, for example, may be selected from the group consisting of natural gas, oil, petroleum, coal, biomass, and combinations thereof.

[0042] Methanol carbonylation processes suitable for production of acetic acid are described in US Patent Nos. 7,208,624, 7,115,772, 7,005,541, 6,657,078, 6,627,770, 6,143,930, 5,599,976, 5,144,068, 5,026,908, 5,001,259, and 4,994,608, all of which are hereby incorporated by reference.

[0043] US Patent No. RE 35,377, which is hereby incorporated by reference, provides a method for the production of methanol by conversion of carbonaceous materials such as oil, coal, natural gas and biomass materials. The process includes hydrogasification of solid and/or liquid carbonaceous materials to obtain a process gas which is steam pyrolized with additional natural gas to form syn gas. The syn gas is converted to methanol which may be carbonylated to acetic acid. US Patent No. 5,821,111, which discloses a process for converting waste biomass through gasification into syn gas, as well as US Patent No. 6,685,754 are hereby incorporated by reference.

[0044] In one optional embodiment, the acetic acid that is utilized in the condensation reaction comprises acetic acid and may also comprise other carboxylic acids, e.g., propionic acid, esters, and anhydrides, as well as acetaldehyde and acetone. In one embodiment, the acetic acid fed to the condensation reaction comprises propionic acid. For example, the acetic acid fed to the reaction may comprise from 0.001 wt.% to 15 wt.% propionic acid, e.g., from 0.001 wt.% to 0.11 wt.%, from 0.125 wt.% to 12.5 wt.%, from 1.25 wt.% to 11.25 wt.%, or from 3.75 wt.% to 8.75 wt.%. Thus, the acetic acid feed stream may be a cruder acetic acid feed stream , e.g., a less-refined acetic acid feed stream.

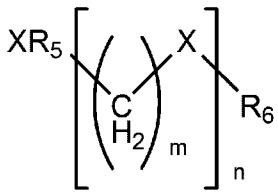
[0045] As used herein, "alkylenating agent" means an aldehyde or precursor to an aldehyde suitable for reacting with the alkanoic acid, e.g., acetic acid, to form an unsaturated acid, e.g., acrylic acid, or an alkyl acrylate. In preferred embodiments, the alkylenating agent comprises a methylenating agent such as formaldehyde, which preferably is capable of adding a methylene group ($=CH_2$) to the organic acid. Other alkylenating agents may include, for example, acetaldehyde, propanal, butanal, aryl aldehydes, benzyl aldehydes, alcohols, and combinations thereof. This listing is not exclusive and is not meant to limit the scope of the invention. In one embodiment, an alcohol may serve as a source of the alkylenating agent. For example, the alcohol may be reacted *in situ* to form the alkylenating agent, e.g., the aldehyde.

[0046] The alkylenating agent, e.g., formaldehyde, may be derived from any suitable source. Exemplary sources may include, for example, aqueous formaldehyde solutions, anhydrous

formaldehyde derived from a formaldehyde drying procedure, trioxane, diether of methylene glycol, and paraformaldehyde. In a preferred embodiment, the formaldehyde is produced via a a methanol oxidation process, which reacts methanol and oxygen to yield the formaldehyde.

[0047] In other embodiments, the alkylenating agent is a compound that is a source of formaldehyde. Where forms of formaldehyde that are not as freely or weakly complexed are used, the formaldehyde will form *in situ* in the condensation reactor or in a separate reactor prior to the condensation reactor. Thus for example, trioxane may be decomposed over an inert material or in an empty tube at temperatures over 350 °C or over an acid catalyst at over 100 °C to form the formaldehyde.

[0048] In one embodiment, the alkylenating agent corresponds to Formula I.



[0049] In this formula, R_5 and R_6 may be independently selected from C_1-C_{12} hydrocarbons, preferably, C_1-C_{12} alkyl, alkenyl or aryl, or hydrogen. Preferably, R_5 and R_6 are independently C_1-C_6 alkyl or hydrogen, with methyl and/or hydrogen being most preferred. X may be either oxygen or sulfur, preferably oxygen; and n is an integer from 1 to 10, preferably 1 to 3. In some embodiments, m is 1 or 2, preferably 1.

[0050] In one embodiment, the compound of formula I may be the product of an equilibrium reaction between formaldehyde and methanol in the presence of water. In such a case, the compound of formula I may be a suitable formaldehyde source. In one embodiment, the formaldehyde source includes any equilibrium composition. Examples of formaldehyde sources include but are not restricted to methylal (1,1 dimethoxymethane); polyoxymethylenes -$(CH_2$-$O)_i$- wherein i is from 1 to 100; formalin; and other equilibrium compositions such as a mixture of formaldehyde, methanol, and methyl propionate. In one embodiment, the source of formaldehyde is selected from the group consisting of 1, 1 dimethoxymethane; higher formals of formaldehyde and methanol; and CH_3-O-$(CH_2$-$O)_i$-CH_3 where i is 2.

[0051] The alkylenating agent may be used with or without an organic or inorganic solvent.

[0052] The term "formalin," refers to a mixture of formaldehyde, methanol, and water. In one embodiment, formalin comprises from 25 wt.% to 65% formaldehyde; from 0.01 wt.% to 25 wt.% methanol; and from 25 wt.% to 70 wt.% water. In cases where a mixture of formaldehyde, methanol, and methyl propionate is used, the mixture comprises less than 10 wt.% water, e.g., less than 5 wt.% or less than 1 wt.%.

[0053] In some embodiments, the condensation reaction may achieve favorable conversion of acetic acid and favorable selectivity and productivity to acrylates. For purposes of the present invention, the term "conversion" refers to the amount of acetic acid in the feed that is converted to a compound other than acetic acid. Conversion is expressed as a percentage based on acetic acid in the feed. The conversion of acetic acid may be at least 10%, e.g., at least 20%, at least 40%, or at least 50%.

[0054] Selectivity, as it refers to the formation of acrylate product, is expressed as the ratio of the amount of carbon in the desired product(s) and the amount of carbon in the total products. This ratio may be multiplied by 100 to arrive at the selectivity. Preferably, the catalyst selectivity to acrylate products, e.g., acrylic acid and methyl acrylate, is at least 40 mol%, e.g., at least 50 mol%, at least 60 mol%, or at least 70 mol%. In some embodiments, the selectivity to acrylic acid is at least 30 mol %, e.g., at least 40 mol%, or at least 50 mol%; and/or the selectivity to methyl acrylate is at least 10 mol%, e.g., at least 15 mol%, or at least 20 mol%.

[0055] The terms "productivity" or "space time yield" as used herein, refers to the grams of a specified product, e.g., acrylate products, formed per hour during the condensation based on the liters of catalyst used . A productivity of at least 20 grams of acrylate product per liter catalyst per hour, e.g., at least 40 grams of acrylates per liter catalyst per hour or at least 100 grams of acrylates per liter catalyst per hour, is preferred. In terms of ranges, the productivity preferably is from 20 to 500 grams of acrylates per liter catalyst per hour, e.g., from 20 to 200 grams of acrylates per liter catalyst per hour or from 40 to 140 grams of acrylates per liter catalyst per hour.

[0056] In one embodiment, the inventive process yields at least 1,800 kg/hr of finished acrylic acid, e.g., at least 3,500 kg/hr, at least 18,000 kg/hr, or at least 37,000 kg/hr.

[0057] Preferred embodiments of the inventive process demonstrate a low selectivity to undesirable products, such as carbon monoxide and carbon dioxide. The selectivity to these undesirable products preferably is less than 29%, e.g., less than 25% or less than 15%. More

preferably, these undesirable products are not detectable. Formation of alkanes, e.g., ethane, may be low, and ideally less than 2%, less than 1%, or less than 0.5% of the acetic acid passed over the catalyst is converted to alkanes, which have little value other than as fuel.

[0058] The alkanoic acid or ester thereof and alkylenating agent may be fed independently or after prior mixing to a reactor containing the catalyst. The reactor may be any suitable reactor or combination of reactors. Preferably, the reactor comprises a fixed bed reactor or a series of fixed bed reactors. In one embodiment, the reactor is a packed bed reactor or a series of packed bed reactors. In one embodiment, the reactor is a fixed bed reactor. Of course, other reactors such as a continuous stirred tank reactor or a fluidized bed reactor, may be employed.

[0059] In some embodiments, the alkanoic acid, e.g., acetic acid, and the alkylenating agent, e.g., formaldehyde, are fed to the reactor at a molar ratio of at least 0.10:1, e.g., at least 0.75:1 or at least 1:1. In terms of ranges the molar ratio of alkanoic acid to alkylenating agent may range from 0.10:1 to 10:1 or from 0.75:1 to 5:1. In some embodiments, the reaction of the alkanoic acid and the alkylenating agent is conducted with a stoichiometric excess of alkanoic acid. In these instances, acrylate selectivity may be improved. As an example the acrylate selectivity may be at least 10% higher than a selectivity achieved when the reaction is conducted with an excess of alkylenating agent, e.g., at least 20% higher or at least 30% higher. In other embodiments, the reaction of the alkanoic acid and the alkylenating agent is conducted with a stoichiometric excess of alkylenating agent.

[0060] The condensation reaction may be conducted at a temperature of at least 250 °C, e.g., at least 300 °C, or at least 350 °C. In terms of ranges, the reaction temperature may range from 200 °C to 500 °C, e.g., from 250 °C to 400 °C, or from 250 °C to 350 °C. The acetic acid conversion, in some embodiments, may vary depending upon the reaction temperature. Residence time in the reactor may range from 1 second to 200 seconds, e.g., from 1 second to 100 seconds. Reaction pressure is not particularly limited, and the reaction is typically performed near atmospheric pressure. In one embodiment, the reaction may be conducted at a pressure ranging from 0 kPa to 4100 kPa, e.g., from 3 kPa to 345 kPa, or from 6 to 103 kPa. Without wishing to be bound by any theory, it is believed that, with chemical kinetics of the reaction chemistry as a driver, reaction efficiency may be improved with lower reactant concentrations (in mol/m^3). Decreased reaction pressure, with corresponding decreased reactant concentrations (i.e., partial pressures), results in greater product yields. In one embodiment,

addition of one or more diluents, e.g., nitrogen and/or carbon dioxide, to the reaction mixture can further reduce reactant concentrations (i.e., partial pressures) in the reaction mixture. While lower operating pressures and/or inclusion of diluent(s) in the reaction mixture will increase product yield, overall production per unit volume of catalyst will be decreased, due to the lower operating pressure and/or dilution of the reaction mixture. Again, without wishing to be bound by any theory, in one embodiment, it is believed that the produced acrylate product(s), for example, acrylic acid, may act as an inhibitor for the catalyst of the presently disclosed process.

[0061] In one embodiment, the reaction is conducted at a gas hourly space velocity ("GHSV") greater than 600 hr^{-1}, e.g., greater than 1000 hr^{-1} or greater than 2000 hr^{-1}. In one embodiment, the GHSV ranges from 600 hr^{-1} to 10000 hr^{-1}, e.g., from 1000 hr^{-1} to 8000 hr^{-1} or from 1500 hr^{-1} to 7500 hr^{-1}. As one particular example, when GHSV is at least 2000 hr^{-1}, the acrylate product STY may be at least 150 g/hr/liter.

[0062] Water may be present in the reactor in amounts up to 60 wt.%, by weight of the reaction mixture, e.g., up to 50 wt.% or up to 40 wt.%. Water, however, is preferably reduced due to its negative effect on process rates and separation costs.

[0063] In one embodiment, an inert or reactive gas, e.g., a diluent, is supplied to the reactant stream. Examples of inert gases include, but are not limited to, nitrogen, helium, argon, and methane. Examples of reactive gases or vapors include, but are not limited to, oxygen, carbon oxides, sulfur oxides, and alkyl halides. When reactive gases such as oxygen are added to the reactor, these gases, in some embodiments, may be added in stages throughout the catalyst bed at desired levels as well as feeding with the other feed components at the beginning of the reactors. The addition of these additional components may improve reaction efficiencies.

[0064] In one embodiment, the unreacted components such as the alkanoic acid and formaldehyde as well as the inert and/or reactive gases that remain are recycled to the reactor after sufficient separation from the desired product.

[0065] When the desired product is an unsaturated ester made by reacting an ester of an alkanoic acid ester with formaldehyde, the alcohol corresponding to the ester may also be fed to the reactor either with or separately to the other components. For example, when methyl acrylate is desired, methanol may be fed to the reactor. The alcohol, amongst other effects, reduces the quantity of acids leaving the reactor. It is not necessary that the alcohol is added at the beginning of the reactor and it may for instance be added in the middle or near the back, in

order to effect the conversion of acids such as propionic acid, methacrylic acid to their respective esters without depressing catalyst activity. In one embodiment, the alcohol may be added downstream of the reactor.

Catalyst Composition

[0066] The catalyst may be any suitable catalyst composition. As one example, condensation catalyst consisting of mixed oxides of vanadium and phosphorus have been investigated and described in M. Ai, *J. Catal.*, 107, 201 (1987); M. Ai, *J. Catal.*, 124, 293 (1990); M. Ai, *Appl. Catal.*, 36, 221 (1988); and M. Ai, Shokubai, 29, 522 (1987). Other examples include binary vanadium-titanium phosphates, vanadium-silica-phosphates, and alkali metal-promoted silicas, e.g., cesium- or potassium-promoted silicas.

[0067] In one embodiment, the inventive process employs a catalyst composition comprising vanadium, titanium, and optionally at least one oxide additive. The oxide additive(s), if present, are preferably present in the active phase of the catalyst. In one embodiment, the oxide additive(s) are selected from the group consisting of silica, alumina, zirconia, and mixtures thereof or any other metal oxide other than metal oxides of titanium or vanadium. Preferably, the molar ratio of oxide additive to titanium in the active phase of the catalyst composition is greater than 0.05:1, e.g., greater than 0.1:1, greater than 0.5:1, or greater than 1:1. In terms of ranges, the molar ratio of oxide additive to titanium in the inventive catalyst may range from 0.05:1 to 20:1, e.g., from 0.1:1 to 10:1, or from 1:1 to 10:1. In these embodiments, the catalyst comprises titanium, vanadium, and one or more oxide additives and have relatively high molar ratios of oxide additive to titanium.

[0068] In another embodiment, the inventive process employs a catalyst comprising vanadium, titanium, bismuth, tungsten, or mixtures thereof. In some embodiments, the catalyst comprises bismuth. In other embodiments, the catalyst comprises tungsten. Exemplary catalyst compositions include vanadium/titanium/bismuth, vanadium/titanium/tungsten, bismuth/tungsten, and vanadium/bismuth/tungsten.

[0069] In other embodiments, the catalyst may further comprise other compounds or elements (metals and/or non-metals). For example, the catalyst may further comprise phosphorus and/or oxygen. In these cases, the catalyst may comprise from 15 wt% to 45 wt% phosphorus, e.g., from 20 wt% to 35 wt% or from 23 wt% to 27 wt%; and/or from 30 wt% to 75 wt% oxygen, e.g., from 35 wt% to 65 wt% or from 48 wt% to 51 wt%.

[0070] In some embodiments, the catalyst further comprises additional metals and/or oxide additives. These additional metals and/or oxide additives may function as promoters. If present, the additional metals and/or oxide additives may be selected from the group consisting of copper, molybdenum, tungsten, nickel, niobium, and combinations thereof. Other exemplary promoters that may be included in the catalyst of the invention include lithium, sodium, magnesium, aluminum, chromium, manganese, iron, cobalt, calcium, yttrium, ruthenium, silver, tin, barium, lanthanum, the rare earth metals, hafnium, tantalum, rhenium, thorium, bismuth, antimony, germanium, zirconium, uranium, cesium, zinc, and silicon and mixtures thereof. Other modifiers include boron, gallium, arsenic, sulfur, halides, Lewis acids such as BF_3, $ZnBr_2$, and $SnCl_4$. Exemplary processes for incorporating promoters into catalyst are described in US Pat. No. 5,364,824, the entirety of which is incorporated herein by reference.

[0071] If the catalyst comprises additional metal(s) and/or metal oxides(s), the catalyst optionally may comprise additional metals and/or metal oxides in an amount from 0.001 wt% to 30 wt%, e.g., from 0.01 wt% to 5 wt% or from 0.1 wt% to 5 wt%. If present, the promoters may enable the catalyst to have a weight/weight space time yield of at least 25 grams of acrylic acid/gram catalyst-h, e.g., least 50 grams of acrylic acid/gram catalyst-h, or at least 100 grams of acrylic acid/gram catalyst-h.

[0072] In some embodiments, the catalyst is unsupported. In these cases, the catalyst may comprise a homogeneous mixture or a heterogeneous mixture as described above. In one embodiment, the homogeneous mixture is the product of an intimate mixture of vanadium and titanium oxides, hydroxides, and phosphates resulting from preparative methods such as controlled hydrolysis of metal alkoxides or metal complexes. In other embodiments, the heterogeneous mixture is the product of a physical mixture of the vanadium and titanium phosphates. These mixtures may include formulations prepared from phosphorylating a physical mixture of preformed hydrous metal oxides. In other cases, the mixture(s) may include a mixture of preformed vanadium pyrophosphate and titanium pyrophosphate powders.

[0073] In another embodiment, the catalyst is a supported catalyst comprising a catalyst support in addition to the vanadium, titanium, oxide additive, and optionally phosphorous and oxygen, in the amounts indicated above (wherein the molar ranges indicated are without regard to the moles of catalyst support, including any vanadium, titanium, oxide additive, phosphorous or oxygen contained in the catalyst support). The total weight of the support (or modified

support), based on the total weight of the catalyst, preferably is from 75 wt.% to 99.9 wt.%, e.g., from 78 wt.% to 97 wt.% or from 80 wt.% to 95 wt.%. The support may vary widely. In one embodiment, the support material is selected from the group consisting of silica, alumina, zirconia, titania, aluminosilicates, zeolitic materials, mixed metal oxides (including but not limited to binary oxides such as SiO_2-Al_2O_3, SiO_2-TiO_2, SiO_2-ZnO, SiO_2-MgO, SiO_2-ZrO_2, Al_2O_3-MgO, Al_2O_3-TiO_2, Al_2O_3-ZnO, TiO_2-MgO, TiO_2-ZrO_2, TiO_2-ZnO, TiO_2-SnO_2) and mixtures thereof, with silica being one preferred support. In embodiments where the catalyst comprises a titania support, the titania support may comprise a major or minor amount of rutile and/or anatase titanium dioxide. Other suitable support materials may include, for example, stable metal oxide-based supports or ceramic-based supports. Preferred supports include silicaceous supports, such as silica, silica/alumina, a Group IIA silicate such as calcium metasilicate, pyrogenic silica, high purity silica, silicon carbide, sheet silicates or clay minerals such as montmorillonite, beidellite, saponite, pillared clays, other microporous and mesoporous materials, and mixtures thereof. Other supports may include, but are not limited to, iron oxide, magnesia, steatite, magnesium oxide, carbon, graphite, high surface area graphitized carbon, activated carbons, and mixtures thereof. These listings of supports are merely exemplary and are not meant to limit the scope of the present invention.

[0074] In some embodiments, a zeolitic support is employed. For example, the zeolitic support may be selected from the group consisting of montmorillonite, NH_4 ferrierite, H-mordenite-PVOx, vermiculite-1, H-ZSM5, NaY, H-SDUSY, Y zeolite with high SAR, activated bentonite, H-USY, MONT-2, HY, mordenite SAR 20, SAPO-34, Aluminosilicate (X), VUSY, Aluminosilicate (CaX), Re-Y, and mixtures thereof. H-SDUSY, VUSY, and H-USY are modified Y zeolites belonging to the faujasite family. In one embodiment, the support is a zeolite that does not contain any metal oxide modifier(s). In some embodiments, the catalyst composition comprises a zeolitic support and the active phase comprises a metal selected from the group consisting of vanadium, aluminum, nickel, molybdenum, cobalt, iron, tungsten, zinc, copper, titanium cesium bismuth, sodium, calcium, chromium, cadmium, zirconium, and mixtures thereof. In some of these embodiments, the active phase may also comprise hydrogen, oxygen, and/or phosphorus.

[0075] In other embodiments, in addition to the active phase and a support, the inventive catalyst may further comprise a support modifier. A modified support, in one embodiment,

relates to a support that includes a support material and a support modifier, which, for example, may adjust the chemical or physical properties of the support material such as the acidity or basicity of the support material. In embodiments that use a modified support, the support modifier is present in an amount from 0.1 wt.% to 50 wt.%, e.g., from 0.2 wt.% to 25 wt.%, from 0.5 wt.% to 15 wt.%, or from 1 wt.% to 8 wt.%, based on the total weight of the catalyst composition.

[0076] In one embodiment, the support modifier is an acidic support modifier. In some embodiments, the catalyst support is modified with an acidic support modifier. The support modifier similarly may be an acidic modifier that has a low volatility or little volatility. The acidic modifiers may be selected from the group consisting of oxides of Group IVB metals, oxides of Group VB metals, oxides of Group VIB metals, iron oxides, aluminum oxides, and mixtures thereof. In one embodiment, the acidic modifier may be selected from the group consisting of WO_3, MoO_3, Fe_2O_3, Cr_2O_3, V_2O_5, MnO_2, CuO, Co_2O_3, Bi_2O_3, TiO_2, ZrO_2, Nb_2O_5, Ta_2O_5, Al_2O_3, B_2O_3, P_2O_5, and Sb_2O_3.

[0077] In another embodiment, the support modifier is a basic support modifier. The presence of chemical species such as alkali and alkaline earth metals, are normally considered basic and may conventionally be considered detrimental to catalyst performance. The presence of these species, however, surprisingly and unexpectedly, may be beneficial to the catalyst performance. In some embodiments, these species may act as catalyst promoters or a necessary part of the acidic catalyst structure such in layered or sheet silicates such as montmorillonite. Without being bound by theory, it is postulated that these cations create a strong dipole with species that create acidity.

[0078] Additional modifiers that may be included in the catalyst include, for example, boron, aluminum, magnesium, zirconium, and hafnium.

[0079] As will be appreciated by those of ordinary skill in the art, the support materials, if included in the catalyst of the present invention, preferably are selected such that the catalyst system is suitably active, selective and robust under the process conditions employed for the formation of the desired product, e.g., acrylic acid or alkyl acrylate. Also, the active metals and/or pyrophosphates that are included in the catalyst of the invention may be dispersed throughout the support, coated on the outer surface of the support (egg shell) or decorated on the surface of the support. In some embodiments, in the case of macro- and meso-porous materials,

the active sites may be anchored or applied to the surfaces of the pores that are distributed throughout the particle and hence are surface sites available to the reactants but are distributed throughout the support particle.

[0080] The inventive catalyst may further comprise other additives, examples of which may include: molding assistants for enhancing moldability; reinforcements for enhancing the strength of the catalyst; pore-forming or pore modification agents for formation of appropriate pores in the catalyst, and binders. Examples of these other additives include stearic acid, graphite, starch, cellulose, silica, alumina, glass fibers, silicon carbide, and silicon nitride. Preferably, these additives do not have detrimental effects on the catalytic performances, e.g., conversion and/or activity. These various additives may be added in such an amount that the physical strength of the catalyst does not readily deteriorate to such an extent that it becomes impossible to use the catalyst practically as an industrial catalyst.

Separation

[0081] The unique diluted liquid acrylate stream of the present invention may be separated in a separation zone to form a final product, e.g., a final acrylic acid product. In one embodiment, the inventive process comprises the step of separating at least a portion of the diluted liquid acrylate stream to form an alkylenating agent stream and an intermediate product stream. This separating step may be referred to as an "akylenating agent split." In one embodiment, the alkylenating agent stream comprises significant amounts of alkylenating agent(s). For example, the alkylenating agent stream may comprise at least 1 wt.% alkylenating agent(s), e.g., at least 5 wt.%, at least 10 wt.%, at least 15 wt.%, or at least 25 wt.%. In terms of ranges, the alkylenating stream may comprise from 1 wt.% to 75 wt.% alkylenating agent(s), e.g., from 3 to 50 wt.%, from 3 wt.% to 25 wt.%, or from 10 wt.% to 20 wt.%. In terms of upper limits, the alkylenating stream may comprise less than 75 wt.% alkylenating agent(s), e.g. less than 50 wt.% or less than 40 wt.%. In preferred embodiments, the alkylenating agent is formaldehyde.

[0082] As noted above, the presence of alkylenating agent in crude acrylate product streams and derivatives thereof adds unpredictability and problems to separation schemes. Without being bound by theory, it is believed that formaldehyde reacts in many side reactions with water to form by-products. The following side reactions are exemplary.

[0083] $CH_2O + H_2O \rightarrow HOCH_2OH$

[0084] $HO(CH_2O)_{i-1}H + HOCH_2OH \rightarrow HO(CH_2O)_iH + H_2O$ for $i > 1$

[0085] Without being bound by theory, it is believed that, in some embodiments, as a result of these reactions, the alkylenating agent, e.g., formaldehyde, acts as a "light" component at higher temperatures and as a "heavy" component at lower temperatures. The reaction(s) are exothermic. Accordingly, the equilibrium constant increases as temperature decreases and decreases as temperature increases. At lower temperatures, the larger equilibrium constant favors methylene glycol and oligomer production and formaldehyde becomes limited, and, as such, behaves as a heavy component. At higher temperatures, the smaller equilibrium constant favors formaldehyde production and methylene glycol becomes limited. As such, formaldehyde behaves as a light component. In view of these difficulties, as well as others, the separation of streams that comprise water and formaldehyde cannot be expected to behave as a typical two-component system. These features contribute to the unpredictability and difficulty of the separation of the unique diluted liquid acrylate stream of the present invention.

[0086] By utilizing the inventive dilution step, the separation of alkylenating agent(s) from the (diluted) liquid acrylate stream is surprisingly and unexpectedly improved, to yield a purified product comprising acrylate product and very low amounts of other impurities.

[0087] In one embodiment, the alkylenating split is performed such that a lower amount of acetic acid is present in the resulting alkylenating stream. Preferably, the alkylenating agent stream comprises little or no acetic acid. As an example, the alkylenating agent stream, in some embodiments, comprises less than 50 wt.% acetic acid, e.g., less than 45 wt.%, less than 25 wt.%, less than 10 wt.%, less than 5 wt.%, less than 3 wt.%, or less than 1 wt.%. Surprisingly and unexpectedly, the present invention provides for the lower amounts of acetic acid in the alkylenating agent stream, which, beneficially reduces or eliminates the need for further treatment of the alkylenating agent stream to remove acetic acid. In some embodiments, the alkylenating agent stream may be treated to remove water therefrom, e.g., to purge water.

[0088] In some embodiments, the alkylenating agent split is performed in at least one column, e.g., at least two columns or at least three columns. Preferably, the alkylenating agent is performed in a two column system. In other embodiments, the alkylenating agent split is performed via contact with an extraction agent. In other embodiments, the alkylenating agent split is performed via precipitation methods, e.g., crystallization, and/or azeotropic distillation. Of course, other suitable separation methods may be employed either alone or in combination with the methods mentioned herein.

[0089] The intermediate product stream comprises acrylate products. In one embodiment, the intermediate product stream comprises a significant portion of acrylate products, e.g., acrylic acid. For example, the intermediate product stream may comprise at least 5 wt.% acrylate products, e.g., at least 25 wt.%, at least 40 wt.%, at least 50 wt.%, or at least 60 wt.%. In terms of ranges, the intermediate product stream may comprise from 5 wt.% to 99 wt.% acrylate products, e.g. from 10 wt.% to 90 wt.%, from 25 wt.% to 75 wt.%, or from 35 wt.% to 65 wt.%. The intermediate product stream, in one embodiment, comprises little if any alkylenating agent. For example, the intermediate product stream may comprise less than 1 wt.% alkylenating agent, e.g., less than 0.1 wt.% alkylenating agent, less than 0.05 wt.%, or less than 0.01 wt.%. In addition to the acrylate products, the intermediate product stream optionally comprises acetic acid, water, propionic acid and other components.

[0090] In some cases, the intermediate acrylate product stream comprises higher amounts of alkylenating agent. For example, in one embodiment, the intermediate acrylate product stream comprises from 1 wt.% to 50 wt.% alkylenating agent, e.g., from 1 wt.% to 10 wt.% or from 5 wt.% to 50 wt.%. In terms of limits, the intermediate acrylate product stream may comprise at least 1 wt.% alkylenating agent, e.g., at least 5 wt.% or at least 10 wt.%.

[0091] In one embodiment, the crude acrylate product is optionally treated, e.g. separated, prior to the separation of alkylenating agent therefrom. In such cases, the treatment(s) occur before the alkylenating agent split is performed. In other embodiments, at least a portion of the intermediate acrylate product stream may be further treated after the alkylenating agent split. As one example, the crude acrylate product may be treated to remove light ends therefrom. This treatment may occur either before or after the alkylenating agent split, preferably before the alkylenating agent split. In some of these cases, the further treatment of the intermediate acrylate product stream may result in derivative streams that may be considered to be additional purified acrylate product streams. In other embodiments, the further treatment of the intermediate acrylate product stream results in at least one finished acrylate product stream.

[0092] In one embodiment, the inventive process operates at a high process efficiency. For example, the process efficiency may be at least 10%, e.g., at least 20% or at least 35%. In one embodiment, the process efficiency is calculated based on the flows of reactants into the reaction zone. The process efficiency may be calculated by the following formula.

$$\text{Process Efficiency} = 2N_{HAcA}/[N_{HOAc} + N_{HCHO} + N_{H2O}]$$

[0093] where:

[0094] N_{HAcA} is the molar production rate of acrylate products; and

[0095] N_{HOAc}, N_{HCHO}, and N_{H2O} are the molar feed rates of acetic acid, formaldehyde, and water.

[0096] As discussed above, the diluted liquid acrylate stream is separated to yield an intermediate acrylate product stream. FIG. 1 is a flow diagram depicting the formation of the diluted liquid acrylate stream and the separation thereof to obtain an intermediate acrylate product stream. Acrylate product system 100 comprises reaction zone 102 and separation zone 104. Reaction zone 102 comprises reactor 106, first diluent feed 107, alkanoic acid feed, e.g., acetic acid feed, 108, alkylenating agent feed, e.g., formaldehyde feed 110, and vaporizer 112.

[0097] Alkanoic acid, e.g., acetic acid, and alkylenating agent, e.g., formaldehyde, are fed to vaporizer 112 via lines 108 and 110, respectively, to create a vapor feed stream, also referred to as a reaction mixture, which exits vaporizer 112 via line 114 and is directed to reactor 106. In one embodiment, lines 108 and 110 may be combined and jointly fed to the vaporizer 112. The temperature of the vapor feed stream in line 114 is preferably from 200°C to 600°C, e.g., from 250°C to 500°C or from 340°C to 425°C. Alternatively, a vaporizer may not be employed and the reactants may be fed directly to reactor 106.

[0098] Any feed that is not vaporized may be removed from vaporizer 112 and may be recycled or discarded. In addition, although line 114 is shown as being directed to the upper half of reactor 106, line 114 may be directed to the middle or bottom of first reactor 106. Further modifications and additional components to reaction zone 102 and separation zone 104 are described below.

[0099] Reactor 106 contains the catalyst that is used in the reaction to form the crude acrylate product, which is withdrawn, preferably continuously, from reactor 106 via line 116. Although FIG. 1 shows the crude acrylate product being withdrawn from the bottom of reactor 106, the crude acrylate product may be withdrawn from any portion of reactor 106. Exemplary composition ranges for the diluted liquid acrylate stream are shown in Table 1 above.

[0100] In one embodiment, one or more guard beds (not shown) may be used upstream of the reactor to protect the catalyst from poisons or undesirable impurities contained in the feed or return/recycle streams. Such guard beds may be employed in the vapor or liquid streams. Suitable guard bed materials may include, for example, carbon, silica, alumina, ceramic, or

resins. In one aspect, the guard bed media is functionalized, e.g., silver functionalized, to trap particular species such as sulfur or halogens.

[0101] The crude acrylate product in line 116 may be separated in light ends removal unit 122 to form liquid acrylate stream in line 116' and purge stream in line 117. Purge stream 117 may comprise inert or reactive gases and by-products, e.g., nitrogen, carbon monoxide, carbon dioxide, argon, helium, and mixtures thereof. At least a portion of purge stream 117 may be purged and at least a portion of purge stream 117 may be either combined with line 114 or fed directly to reactor 106 (not shown). Liquid acrylate stream 116' is diluted with diluent via line 115 to form diluted liquid acrylate stream in line 119. Diluted liquid acrylate stream 119 is then fed to separation zone 104. Separation zone 104 may comprise one or more separation units, e.g., two or more or three or more. In one example, separation zone 104 contains multiple columns, as shown in FIGS. 2 and 3. Separation zone 104 separates the liquid acrylate stream into at least one intermediate acrylate product stream, which exits via line 118 and at least one alkylenating agent stream, which exits via line 120. Separation zone 104 also separates the liquid acrylate stream into at least one acetic acid stream, which exits via line 121. This acetic acid stream may be combined with diluent 115. In some embodiments, line 121 is the sole source for line 115. Exemplary compositional ranges for the intermediate acrylate product stream are shown in Table 2. Components other than those listed in Table 2 may also be present in the intermediate acrylate product stream. Examples include methanol, methyl acetate, methyl acrylate, dimethyl ketone, carbon dioxide, carbon monoxide, oxygen, nitrogen, and acetone.

TABLE 2
INTERMEDIATE ACRYLATE PRODUCT STREAM COMPOSITION

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Acrylic Acid	at least 5	5 to 99	35 to 65
Acetic Acid	less than 95	5 to 90	50 to 70
Water	less than 75	0.1 to 70	0.5 to 60
Alkylenating Agent	< 1	< 0.5	< 0.1
Propionic Acid	< 10	0.01 to 5	0.01 to 1

[0102] In other embodiments, the intermediate acrylate product stream comprises higher amounts of alkylenating agent. For example, the intermediate acrylate product stream may comprise from 1 wt.% to 10 wt.% alkylenating agent, e.g., from 1 wt.% to 8 wt.% or from 2

wt.% to 5 wt.%. In one embodiment, the intermediate acrylate product stream comprises greater than 1 wt.% alkylenating agent, e.g., greater than 5 wt.% or greater than 10 wt.%.

[0103] Exemplary compositional ranges for the alkylenating agent stream are shown in Table 3. Components other than those listed in Table 3 may also be present in the purified alkylate product stream. Examples include methanol, methyl acetate, methyl acrylate, dimethyl ketone, carbon dioxide, carbon monoxide, oxygen, nitrogen, and acetone.

TABLE 3
ALKYLENATING AGENT STREAM COMPOSITION

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Acrylic Acid	less than 15	0.01 to 10	0.1 to 5
Acetic Acid	10 to 65	20 to 65	25 to 55
Water	15 to 75	25 to 65	30 to 60
Alkylenating Agent	at least 1	1 to 75	10 to 20
Propionic Acid	< 10	0.001 to 5	0.001 to 1

[0104] In other embodiments, the alkylenating stream comprises lower amounts of acetic acid. For example, the alkylenating agent stream may comprise less than 10 wt.% acetic acid, e.g., less than 5 wt.% or less than 1 wt.%.

[0105] As mentioned above, the diluted liquid acrylate stream of the present invention comprises little, if any, furfural and/or acrolein. As such the derivative stream(s) of the diluted liquid acrylate stream will comprise little, if any, furfural and/or acrolein. In one embodiment, the derivative stream(s), e.g., the streams of the separation zone, comprises less than less than 500 wppm acrolein, e.g., less than 100 wppm, less than 50 wppm, or less than 10 wppm. In one embodiment, the derivative stream(s) comprises less than less than 500 wppm furfural, e.g., less than 100 wppm, less than 50 wppm, or less than 10 wppm.

[0106] FIG. 2 shows an overview of a reaction/separation scheme in accordance with the present invention. Acrylate product system 200 comprises reaction zone 202 and separation zone 204. Reaction zone 202 comprises reactor 206, alkanoic acid feed, e.g., acetic acid feed, 208, alkylenating agent feed, e.g., formaldehyde feed, 210, vaporizer 212, and line 214. Reaction zone 202 and the components thereof function in a manner similar to reaction zone 102 of FIG. 1.

[0107] Reaction zone 202 yields a crude acrylate product, which exits reaction zone 202 via line 216 and is directed to separation zone 204. The components of the crude acrylate product are

discussed above. Separation zone 204 comprises alkylenating agent split unit 232, acrylate product split unit 234, acetic acid split unit 236, and drying unit 238. Separation zone 204 may also comprise a light ends removal unit 222. For example, the light ends removal unit may comprise a condenser and/or a flasher. The light ends removal unit may be configured upstream of the alkylenating agent split unit. Depending on the configuration, the light ends removal unit removes light ends from the crude acrylate stream, the alkylenating stream, and/or the intermediate acrylate product stream. In one embodiment, when the light ends are removed, the remaining liquid phase comprises the acrylic acid, acetic acid, alkylenating agent, and/or water. As shown in FIG. 2, the crude acrylate product in line 216 may be separated in light ends removal unit 222 to form liquid acrylate stream in line 216' and purge stream in line 217 as discussed above. Liquid acrylate stream 216' is then diluent with diluent in line 215 to form diluted liquid acrylate stream in line 219. Diluted liquid acrylate stream 219 may then be fed to alkylenating agent split unit 232.

[0108] Alkylenating agent split unit 232 may comprise any suitable separation device or combination of separation devices. For example, alkylenating agent split unit 232 may comprise a column, e.g., a standard distillation column, an extractive distillation column and/or an azeotropic distillation column. In other embodiments, alkylenating agent split unit 232 comprises a precipitation unit, e.g., a crystallizer and/or a chiller. Preferably, alkylenating agent split unit 232 comprises two standard distillation columns. In another embodiment, the alkylenating agent split is performed by contacting the diluted liquid acrylate stream with a solvent that is immiscible with water. For example alkylenating agent split unit 232 may comprise at least one liquid-liquid extraction columns. In another embodiment, the alkylenating agent split is performed via azeotropic distillation, which employs an azeotropic agent. In these cases, the azeotropic agent may be selected from the group consisting of methyl isobutylketene, o-xylene, toluene, benzene, n-hexane, cyclohexane, p-xylene, and mixtures thereof. This listing is not exclusive and is not meant to limit the scope of the invention. In another embodiment, the alkylenating agent split is performed via a combination of distillation, e.g., standard distillation, and crystallization. Of course, other suitable separation devices may be employed either alone or in combination with the devices mentioned herein.

[0109] In FIG. 2, alkylenating agent split unit 232 comprises first column 244 and second column 246. Alkylenating agent split unit 232 receives crude acrylic product stream in line 216

and separates same into at least one alkylenating agent stream, e.g., stream 248, and at least one purified product stream, e.g., stream 242. Alkylenating agent split unit 232 performs an alkylenating agent split, as discussed above.

[0110] In operation, as shown in FIG. 2, the diluted liquid acrylate stream in line 219 is directed to first column 244. First column 244 separates the diluted liquid acrylate stream into a distillate in line 240 and a residue in line 242. The distillate may be refluxed and the residue may be boiled up as shown. In some embodiments, acetic acid from residue 242 may be recycled to be used as diluent in line 215. Stream 240 comprises at least 1 wt.% alkylenating agent. As such, stream 240 may be considered an alkylenating agent stream. The first column residue exits first column 244 in line 242 and comprises a significant portion of acrylate product. As such, stream 242 is an intermediate product stream. Exemplary compositional ranges for the distillate and residue of first column 244 are shown in Table 4. Components other than those listed in Table 4 may also be present in the residue and distillate.

TABLE 4
FIRST COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	0.1 to 20	1 to 10	1 to 5
Acetic Acid	25 to 65	35 to 55	40 to 50
Water	15 to 55	25 to 45	30 to 40
Alkylenating Agent	at least 1	1 to 75	10 to 20
Propionic Acid	< 10	0.001 to 5	0.001 to 1
Residue			
Acrylic Acid	at least 5	5 to 99	35 to 65
Acetic Acid	less than 95	5 to 90	20 to 60
Water	less than 25	0.1 to 10	0.5 to 7
Alkylenating Agent	< 1	< 0.5	< 0.1
Propionic Acid	< 10	0.01 to 5	0.01 o 1

[0111] In one embodiments, the first distillate comprises smaller amounts of acetic acid, e.g., less than 25 wt.%, less than 10 wt.% , e.g., less than 5 wt.% or less than 1 wt.%.

[0112] In other embodiments, the intermediate acrylate product stream comprises higher amounts of alkylenating agent, e.g., greater than 1 wt.% greater than 5 wt.% or greater than 10 wt.%.

[0113] For convenience, the distillate and residue of the first column may also be referred to as the "first distillate" or "first residue." The distillates or residues of the other columns may also be referred to with similar numeric modifiers (second, third, etc.) in order to distinguish them from one another, but such modifiers should not be construed as requiring any particular separation order.

[0114] In one embodiment, polymerization inhibitors and/or anti-foam agents may be employed in the separation zone, e.g., in the units of the separation zone. The inhibitors may be used to reduce the potential for fouling caused by polymerization of acrylates. The anti-foam agents may be used to reduce potential for foaming in the various streams of the separation zone. The polymerization inhibitors and/or the anti-foam agents may be used at one or more locations in the separation zone.

[0115] Returning to FIG. 2, at least a portion of stream 240 is directed to second column 246. Second column 246 separates the at least a portion of stream 240 into a distillate in line 248 and a residue in line 250. The distillate may be refluxed and the residue may be boiled up as shown. The distillate comprises at least 1 wt.% alkylenating agent. Stream 248, like stream 240, may be considered an alkylenating agent stream. The second column residue exits second column 246 in line 250 and comprises a significant portion of acetic acid. At least a portion of line 250 may be returned to first column 244 for further separation. In one embodiment, at least a portion of line 250 is returned, either directly or indirectly, to reactor 206. Exemplary compositional ranges for the distillate and residue of second column 246 are shown in Table 5. Components other than those listed in Table 5 may also be present in the residue and distillate.

TABLE 5
SECOND COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	0.01 to 10	0.05 to 5	0.1 to 0.5
Acetic Acid	10 to 50	20 to 40	25 to 35
Water	35 to 75	45 to 65	50 to 60
Alkylenating Agent	at least 1	1 to 75	10 to 20
Propionic Acid	0.01 to 10	0.01 to 5	0.01 to 0.05
Residue			
Acrylic Acid	0.1 to 25	0.05 to 15	1 to 10
Acetic Acid	40 to 80	50 to 70	55 to 65
Water	1 to 40	5 to 35	10 to 30
Alkylenating Agent	at least 1	1 to 75	10 to 20
Propionic Acid	< 10	0.001 to 5	0.001 to 1

[0116] In cases where any of the alkylenating agent split unit comprises at least one column, the column(s) may be operated at suitable temperatures and pressures. In one embodiment, the temperature of the residue exiting the column(s) ranges from 90°C to 130°C, e.g., from 95°C to 120°C or from 100°C to 115°C. The temperature of the distillate exiting the column(s) preferably ranges from 60°C to 90°C, e.g., from 65°C to 85°C or from 70°C to 80°C. The pressure at which the column(s) are operated may range from 1 kPa to 300 kPa, e.g., from 10 kPa to 100 kPa or from 40 kPa to 80 kPa. In preferred embodiments, the pressure at which the column(s) are operated is kept at a low level e.g., less than 100 kPa, less than 80 kPa, or less than 60 kPa. In terms of lower limits, the column(s) may be operated at a pressures of at least 1 kPa, e.g., at least 20 kPa or at least 40 kPa. Without being bound by theory, it is believed that alkylenating agents, e.g., formaldehyde, may not be sufficiently volatile at lower pressures. Thus, maintenance of the column pressures at these levels surprisingly and unexpectedly provides for efficient separation operations. In addition, it has surprisingly and unexpectedly been found that be maintaining a low pressure in the columns of alkylenating agent split unit 232 may inhibit and/or eliminate polymerization of the acrylate products, e.g., acrylic acid, which may contribute to fouling of the column(s).

[0117] In one embodiment, the alkylenating agent split is achieved via one or more liquid-liquid extraction units. Preferably, the one or more liquid-liquid extraction units employ one or more

extraction agents. Multiple liquid-liquid extraction units may be employed to achieve the alkylenating agent split. Any suitable liquid-liquid extraction devices used for multiple equilibrium stage separations may be used. Also, other separation devices, e.g., traditional columns, may be employed in conjunction with the liquid-liquid extraction unit(s).

[0118] In one embodiment (not shown), the diluted liquid acrylate stream is fed to a liquid-liquid extraction column where the diluted liquid acrylate stream is contacted with an extraction agent, e.g., an organic solvent. The liquid-liquid extraction column extracts the acids, e.g., acrylic acid and acetic acid, from the diluted liquid acrylate stream. An aqueous stage comprising water, alkylenating agent, and some acetic acid exits the liquid-liquid extraction unit. Small amounts of acylic acid may also be present in the aqueous stream. The aqueous phase may be further treated and/or recycled. An organic phase comprising acrylic acid, acetic acid, and the extraction agent also exits the liquid-liquid extraction unit. The organic phase may also comprise water and formaldehyde. The acrylic acid may be separated from the organic phase and collected as product. The acetic acid may be separated then recycled and/or used elsewhere. The solvent may be recovered and recycled to the liquid-liquid extreaction unit.

[0119] The inventive process further comprises the step of separating the intermediate acrylate product stream to form a finished acrylate product stream and a first finished acetic acid stream. The finished acrylate product stream comprises acrylate product(s) and the first finished acetic acid stream comprises acetic acid. The separation of the acrylate products from the intermediate product stream to form the finished acrylate product may be referred to as the "acrylate product split."

[0120] Returning to FIG. 2, purified product stream 242 exits alkylenating agent split unit 232 and is directed to acrylate product split unit 234 for further separation, e.g., to further separate the acrylate products therefrom. Acrylate product split unit 234 may comprise any suitable separation device or combination of separation devices. For example, acrylate product split unit 234 may comprise at least one column, e.g., a standard distillation column, an extractive distillation column and/or an azeotropic distillation column. In other embodiments, acrylate product split unit 234 comprises a precipitation unit, e.g., a crystallizer and/or a chiller. Preferably, acrylate product split unit 234 comprises two standard distillation columns as shown in FIG. 2. In another embodiment, acrylate product split unit 234 comprises a liquid-liquid

extraction unit. Of course, other suitable separation devices may be employed either alone or in combination with the devices mentioned herein.

[0121] In FIG. 2, acrylate product split unit 234 comprises third column 252 and fourth column 254. Acrylate product split unit 234 receives at least a portion of purified acrylic product stream in line 242 and separates same into finished acrylate product stream 256 and at least one acetic acid-containing stream. As such, acrylate product split unit 234 may yield the finished acrylate product.

[0122] As shown in FIG. 2, at least a portion of purified acrylic product stream in line 242 is directed to third column 252. Third column 252 separates the purified acrylic product stream to form third distillate, e.g., line 258, and third residue, which is the finished acrylate product stream, e.g., line 256. The distillate may be refluxed and the residue may be boiled up as shown. In some embodiments, at least a portion of stream 256 is recycled to line 215.

[0123] Stream 258 comprises acetic acid and some acrylic acid. In some embodiments, at least a portion of stream 258 is recycled to line 215. The third column residue exits third column 252 in line 256 and comprises a significant portion of acrylate product. As such, stream 256 is a finished product stream. Exemplary compositional ranges for the distillate and residue of third column 252 are shown in Table 6. Components other than those listed in Table 6 may also be present in the residue and distillate.

TABLE 6
THIRD COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	0.1 to 40	1 to 30	5 to 30
Acetic Acid	60 to 99	70 to 90	75 to 85
Water	0.1 to 25	0.1 to 10	1 to 5
Alkylenating Agent	less than 1	0.001 to 1	0.1 to 1
Propionic Acid	< 10	0.001 to 5	0.001 to 1
Residue			
Acrylic Acid	at least 85	85 to 99.9	95 to 99.5
Acetic Acid	less than 15	0.1 to 10	0.1 to 5
Water	less than 1	less than 0.1	less than 0.01
Alkylenating Agent	less than 1	0.001 to 1	0.1 to 1
Propionic Acid	0.1 to 10	0.1 to 5	0.5 to 3

[0124] Returning to FIG. 2, at least a portion of stream 258 is directed to fourth column 254. Fourth column 254 separates the at least a portion of stream 258 into a distillate in line 260 and a residue in line 262. The distillate may be refluxed and the residue may be boiled up as shown. The distillate comprises a major portion of acetic acid. In one embodiment, at least a portion of line 260 is returned, either directly or indirectly, to reactor 206. The fourth column residue exits fourth column 254 in line 262 and comprises acetic acid and some acrylic acid. At least a portion of line 262 may be returned to third column 252 for further separation. In one embodiment, at least a portion of line 262 is returned, either directly or indirectly, to reactor 206. In another embodiment, at least a portion of the acetic acid-containing stream in either or both of lines 260 and 262 may be directed to an ethanol production system that utilizes the hydrogenation of acetic acid form the ethanol. In another embodiment, at least a portion of the acetic acid-containing stream in either or both of lines 260 and 262 may be directed to a vinyl acetate system that utilizes the reaction of ethylene, acetic acid, and oxygen form the vinyl acetate. In some embodiments, at least a portion of the acetic acid-containing stream in either or both of lines 260 and 262 may be recycled to line 215. In a preferred embodiment, at least a portion of line 260 is recycled to line 215. Exemplary compositional ranges for the distillate and residue of fourth column 254 are shown in Table 7. Components other than those listed in Table 7 may also be present in the residue and distillate.

TABLE 7
FOURTH COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	0.01 to 10	0.05 to 5	0.1 to 1
Acetic Acid	50 to 99.9	70 to 99.5	80 to 99
Water	0.1 to 25	0.1 to 15	1 to 10
Alkylenating Agent	less than 10	0.001 to 5	0.01 to 5
Propionic Acid	0.0001 to 10	0.001 to 5	0.001 to 0.05
Residue			
Acrylic Acid	5 to 50	15 to 40	20 to 35
Acetic Acid	50 to 95	60 to 80	65 to 75
Water	0.01 to 10	0.01 to 5	0.1 to 1
Alkylenating Agent	less than 1	0.001 to 1	0.1 to 1
Propionic Acid	< 10	0.001 to 5	0.001 to 1

[0125] In cases where the acrylate product split unit comprises at least one column, the column(s) may be operated at suitable temperatures and pressures. In one embodiment, the temperature of the residue exiting the column(s) ranges from 90°C to 130°C, e.g., from 95°C to 120°C or from 100°C to 115°C. The temperature of the distillate exiting the column(s) preferably ranges from 60°C to 90°C, e.g., from 65°C to 85°C or from 70°C to 80°C. The pressure at which the column(s) are operated may range from 1 kPa to 300 kPa, e.g., from 10 kPa to 100 kPa or from 40 kPa to 80 kPa. In preferred embodiments, the pressure at which the column(s) are operated is kept at a low level e.g., less than 50 kPa, less than 27 kPa, or less than 20 kPa. In terms of lower limits, the column(s) may be operated at a pressures of at least 1 kPa, e.g., at least 3 kPa or at least 5 kPa. Without being bound by theory, it has surprisingly and unexpectedly been found that be maintaining a low pressure in the columns of acrylate product split unit 234 may inhibit and/or eliminate polymerization of the acrylate products, e.g., acrylic acid, which may contribute to fouling of the column(s).

[0126] It has also been found that, surprisingly and unexpectedly, maintaining the temperature of acrylic acid-containing streams fed to acrylate product split unit 234 at temperatures below 140°C, e.g., below 130°C or below 115°C, may inhibit and/or eliminate polymerization of acrylate products. In one embodiment, to maintain the liquid temperature at these temperatures, the pressure of the column(s) is maintained at or below the pressures mentioned above. In these cases, due to the lower pressures, the number of theoretical column trays is kept at a low level, e.g., less than 10, less than 8, less than 7, or less than 5. As such, it has surprisingly and unexpectedly been found that multiple columns having fewer trays inhibit and/or eliminate acrylate product polymerization. In contrast, a column having a higher amount of trays, e.g., more than 10 trays or more than 15 trays, would suffer from fouling due to the polymerization of the acrylate products. Thus, in a preferred embodiment, the acrylic acid split is performed in at least two, e.g., at least three, columns, each of which have less than 10 trays, e.g. less than 7 trays. These columns each may operate at the lower pressures discussed above.

[0127] The inventive process further comprises the step of separating an alkylenating agent stream to form a purified alkylenating stream and a purified acetic acid stream. The purified alkylenating agent stream comprises a significant portion of alkylenating agent, and the purified acetic acid stream comprises acetic acid and water. The separation of the alkylenating agent from the acetic acid may be referred to as the "acetic acid split."

[0128] Returning to FIG. 2, alkylenating agent stream 248 exits alkylenating agent split unit 232 and is directed to acetic acid split unit 236 for further separation, e.g., to further separate the alkylenating agent and the acetic acid therefrom. Acetic acid split unit 236 may comprise any suitable separation device or combination of separation devices. For example, acetic acid split unit 236 may comprise at least one column, e.g., a standard distillation column, an extractive distillation column and/or an azeotropic distillation column. In other embodiments, acetic acid split unit 236 comprises a precipitation unit, e.g., a crystallizer and/or a chiller. Preferably, acetic acid split unit 236 comprises a standard distillation column as shown in FIG. 2. In another embodiment, acetic acid split unit 236 comprises a liquid-liquid extraction unit. Of course, other suitable separation devices may be employed either alone or in combination with the devices mentioned herein.

[0129] In FIG. 2, acetic acid split unit 236 comprises fifth column 264. Acetic acid split unit 236 receives at least a portion of alkylenating agent stream in line 248 and separates same into a fifth distillate comprising alkylenating agent in line 266, e.g., a purified alkylenating stream, and a fifth residue comprising acetic acid in line 268, e.g., a purified acetic acid stream. The distillate may be refluxed and the residue may be boiled up as shown. In one embodiment, at least a portion of line 266 and/or line 268 are returned, either directly or indirectly, to reactor 206. At least a portion of stream in line 268 may be further separated. In another embodiment, at least a portion of the acetic acid-containing stream in line 268 may be directed to an ethanol production system that utilizes the hydrogenation of acetic acid form the ethanol. In another embodiment, at least a portion of the acetic acid-containing stream in lines 268 may be directed to a vinyl acetate system that utilizes the reaction of ethylene, acetic acid, and oxygen form the vinyl acetate. In some preferred embodiments, at least a portion of the acetic acid-containing stream in line 268 may be recycled to line 215.

[0130] The stream in line 266 comprises alkylenating agent and water. The stream in line 268 comprises acetic acid and water. Exemplary compositional ranges for the distillate and residue of fifth column 264 are shown in Table 8. Components other than those listed in Table 8 may also be present in the residue and distillate.

TABLE 8
FIFTH COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	less than 1	0.001 to 5	0.001 to 1
Acetic Acid	less than 1	0.001 to 5	0.001 to 1
Water	40 to 80	50 to 70	55 to 65
Alkylenating Agent	20 to 60	30 to 50	35 to 45
Propionic Acid	less than 10	0.001 to 5	0.001 to 1
Residue			
Acrylic Acid	less than 1	0.01 to 5	0.1 to 1
Acetic Acid	25 to 65	35 to 55	40 to 50
Water	35 to 75	45 to 65	50 to 60
Alkylenating Agent	less than 1	0.01 to 5	0.1 to 1
Propionic Acid	less than 1	0.001 to 5	0.01 1

[0131] In cases where the acetic acid split unit comprises at least one column, the column(s) may be operated at suitable temperatures and pressures. In one embodiment, the temperature of the residue exiting the column(s) ranges from 90°C to 130°C, e.g., from 95°C to 120°C or from 100°C to 115°C. The temperature of the distillate exiting the column(s) preferably ranges from 60°C to 90°C, e.g., from 65°C to 85°C or from 70°C to 80°C. The pressure at which the column(s) are operated may range from 1 kPa to 500 kPa, e.g., from 25 kPa to 400 kPa or from 100 kPa to 300 kPa.

[0132] The inventive process further comprises the step of separating the purified acetic acid stream to form a second finished acetic acid stream and a water stream. The second finished acetic acid stream comprises a major portion of acetic acid, and the water stream comprises mostly water. The separation of the acetic from the water may be referred to as dehydration.

[0133] Returning to FIG. 2, fifth residue 268 exits acetic acid split unit 236 and is directed to drying unit 238 for further separation, e.g., to remove water from the acetic acid. Drying unit 238 may comprise any suitable separation device or combination of separation devices. For example, drying unit 238 may comprise at least one column, e.g., a standard distillation column, an extractive distillation column and/or an azeotropic distillation column. In other embodiments, drying unit 238 comprises a dryer and/or a molecular sieve unit. In a preferred embodiment, drying unit 238 comprises a liquid-liquid extraction unit. In one embodiment, drying unit 238 comprises a standard distillation column as shown in FIG. 2. Of course, other

suitable separation devices may be employed either alone or in combination with the devices mentioned herein.

[0134] In FIG. 2, drying unit 238 comprises sixth column 270. Drying unit 238 receives at least a portion of second finished acetic acid stream in line 268 and separates same into a sixth distillate comprising a major portion of water in line 272 and a sixth residue comprising acetic acid and small amounts of water in line 274. The distillate may be refluxed and the residue may be boiled up as shown. In one embodiment, at least a portion of line 274 is returned, either directly or indirectly, to reactor 206. In another embodiment, at least a portion of the acetic acid-containing stream in line 274 may be directed to an ethanol production system that utilizes the hydrogenation of acetic acid form the ethanol. In another embodiment, at least a portion of the acetic acid-containing stream in line 274 may be directed to a vinyl acetate system that utilizes the reaction of ethylene, acetic acid, and oxygen form the vinyl acetate. In some embodiments, at least a portion of the acetic acid-containing stream in line 274 may be recycled to line 215. In other embodiments, at least a portion of sixth distillate 272 is recycled to line 215.

[0135] Exemplary compositional ranges for the distillate and residue of sixth column 270 are shown in Table 9. Components other than those listed in Table 9 may also be present in the residue and distillate.

TABLE 9
SIXTH COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	less than 1	0.001 to 5	0.001 to 1
Acetic Acid	less than 1	0.01 to 5	0.01 to 1
Water	90 to 99.9	95 to 99.9	95 to 99.5
Alkylenating Agent	less than 1	0.01 to 5	0.01 to 1
Propionic Acid	less than 10	0.001 to 5	0.001 to 1
Residue			
Acrylic Acid	less than 1	0.01 to 5	0.01 to 1
Acetic Acid	75 to 99.9	85 to 99.5	90 to 99.5
Water	25 to 65	35 to 55	40 to 50
Alkylenating Agent	less than 1	less than 0.001	less than 0.0001
Propionic Acid	less than 1	0.001 to 5	0.01 1

[0136] In cases where the drying unit comprises at least one column, the column(s) may be operated at suitable temperatures and pressures. In one embodiment, the temperature of the

residue exiting the column(s) ranges from 90°C to 130°C, e.g., from 95°C to 120°C or from 100°C to 115°C. The temperature of the distillate exiting the column(s) preferably ranges from 60°C to 90°C, e.g., from 65°C to 85°C or from 70°C to 80°C. The pressure at which the column(s) are operated may range from 1 kPa to 500 kPa, e.g., from 25 kPa to 400 kPa or from 100 kPa to 300 kPa. FIG. 2 also shows tank 276, which, collects at least one of the process streams prior to recycling same to reactor 206. Tank 276 is an optional feature. The various recycle streams that may, alternatively, be recycled directly to reactor 206 without being collected in tank 276.

[0137] FIG. 3 shows an overview of an alternative reaction/separation scheme in accordance with the present invention.

[0138] Acrylate product system 300 comprises reaction zone 302 and separation zone 304. Reaction zone 302 comprises reactor 306, alkanoic acid feed, e.g., acetic acid feed, 308, alkylenating agent feed, e.g., formaldehyde feed, 310, vaporizer 312, and line 314. Reaction zone 302 and the components thereof function in a manner similar to reaction zone 102 of FIG. 1. Reaction zone 302 also comprises line 313. Line 313 comprises water and may be fed to column 370, discussed below.

[0139] Reaction zone 302 yields a crude acrylate product, which exits reaction zone 302 via line 316 and is directed to separation zone 304. Separation zone 304 comprises alkylenating agent split unit 332, acrylate product split unit 334, drying unit 336, and methanol removal unit 338. Separation zone 304 may also comprise a light ends removal unit 322. For example, the light ends removal unit may comprise a condenser and/or a flasher. The light ends removal unit may be configured either upstream of alkylenating agent split unit 332 or downstream (not shown). Depending on the configuration, the light ends removal unit removes light ends from the crude acrylate product, the alkylenating stream, and/or the intermediate acrylate product stream. In one embodiment, when the light ends are removed, the remaining liquid phase comprises the acrylic acid, acetic acid, alkylenating agent, and/or water. As shown in FIG. 3, line 316 may be separated in light ends removal unit 322 to form purge stream 317 and liquid acrylate stream 316'. The components of the liquid acrylate stream are discussed above. Liquid acrylate stream 316' may then be diluted with diluent in line 315 to form diluted liquid acrylate stream 319.

[0140] Alkylenating agent split unit 332 may comprise any suitable separation device or combination of separation devices. For example, alkylenating agent split unit 332 may comprise

a column, e.g., a standard distillation column, an extractive distillation column and/or an azeotropic distillation column. In other embodiments, alkylenating agent split unit 332 comprises a precipitation unit, e.g., a crystallizer and/or a chiller. Preferably, alkylenating agent split unit 332 comprises a single distillation column.

[0141] In another embodiment, the alkylenating agent split is performed by contacting the diluted liquid acrylate stream with a solvent that is immiscible with water. For example, alkylenating agent split unit 332 may comprise at least one liquid-liquid extraction column. In another embodiment, the alkylenating agent split is performed via azeotropic distillation, which employs an azeotropic agent. In these cases, the azeotropic agent may be selected from the group consisting of methyl isobutylketene, o-xylene, toluene, benzene, n-hexane, cyclohexane, p-xylene, and mixtures thereof. This listing is not exclusive and is not meant to limit the scope of the invention. In another embodiment, the alkylenating agent split is performed via a combination of distillations, e.g., standard distillation, and crystallization. Of course, other suitable separation devices may be employed either alone or in combination with the devices mentioned herein.

[0142] In FIG. 3, alkylenating agent split unit 332 comprises first column 344. The diluted liquid acrylate stream in line 316 is directed to first column 344. First column 344 separates the diluted liquid acrylate stream to form a distillate in line 340 and a residue in line 342. The distillate may be refluxed and the residue may be boiled up as shown. Stream 340 comprises at least 1 wt.% alkylenating agent. As such, stream 340 may be considered an alkylenating agent stream. The first column residue exits first column 344 in line 342 and comprises a significant portion of acrylate product. As such, stream 342 is an intermediate product stream. In some embodiments, at least a portion of stream 342 may be recycled to line 315. In one embodiment, at least a portion of stream 340 is directed to drying column 336.

[0143] Exemplary compositional ranges for the distillate and residue of first column 344 are shown in Table 10. Components other than those listed in Table 10 may also be present in the residue and distillate.

TABLE 10
FIRST COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	less than 5	less than 3	0.05 to 1
Acetic Acid	less than10	less than 5	0.5 to 3
Water	40 to 90	45 to 85	50 to 80
Alkylenating Agent	at least 1	1 to 75	10 to 40
Propionic Acid	less than 10	less than 5	less than 1
Methanol	less than 5	less than 1	less than 0.5
Residue			
Acrylic Acid	10 to 80	15 to 65	20 to 50
Acetic Acid	40 to 80	45 to 70	50 to 65
Water	1 to 40	1 to 20	1 to 10
Alkylenating Agent	less than 50	0.1 to 50	0.1 to 10
Propionic Acid	less than 10	less than 5	less than 1

[0144] In one embodiment, the first distillate comprises smaller amounts of acetic acid, e.g., 25 wt.%, less than 10 wt.%, less than 5 wt.% or less than 1 wt.%. In one embodiment, the first residue comprises larger amounts of alkylenating agent.

[0145] In some embodiments, the intermediate acrylate product stream comprises higher amounts of alkylenating agent, e.g., greater than 1 wt.% greater than 5 wt.% or greater than 10 wt.%.

[0146] In one embodiment, polymerization inhibitors and/or anti-foam agents may be employed in the separation zone, e.g., in the units of the separation zone. The inhibitors may be used to reduce the potential for fouling caused by polymerization of acrylates. The anti-foam agents may be used to reduce potential for foaming in the various streams of the separation zone. The polymerization inhibitors and/or the anti-foam agents may be used at one or more locations in the separation zone.

[0147] In cases where any of alkylenating agent split unit 332 comprises at least one column, the column(s) may be operated at suitable temperatures and pressures. In one embodiment, the temperature of the residue exiting the column(s) ranges from 90°C to 130°C, e.g., from 95°C to 120°C or from 100°C to 115°C. The temperature of the distillate exiting the column(s) preferably ranges from 60°C to 90°C, e.g., from 65°C to 85°C or from 70°C to 80°C. The pressure at which the column(s) are operated may range from 1 kPa to 300 kPa, e.g., from 10 kPa to 100 kPa or from 40 kPa to 80 kPa. In preferred embodiments, the pressure at which the

column(s) are operated is kept at a low level e.g., less than 100 kPa, less than 80 kPa, or less than 60 kPa. In terms of lower limits, the column(s) may be operated at a pressures of at least 1 kPa, e.g., at least 20 kPa or at least 40 kPa. Without being bound by theory, it is believed that alkylenating agents, e.g., formaldehyde, may not be sufficiently volatile at lower pressures. Thus, maintenance of the column pressures at these levels surprisingly and unexpectedly provides for efficient separation operations. In addition, it has surprisingly and unexpectedly been found that by maintaining a low pressure in the columns of alkylenating agent split unit 332 may inhibit and/or eliminate polymerization of the acrylate products, e.g., acrylic acid, which may contribute to fouling of the column(s).

[0148] In one embodiment, the alkylenating agent split is achieved via one or more liquid-liquid extraction units. Preferably, the one or more liquid-liquid extraction units employ one or more extraction agents. Multiple liquid-liquid extraction units may be employed to achieve the alkylenating agent split. Any suitable liquid-liquid extraction devices used for multiple equilibrium stage separations may be used. Also, other separation devices, e.g., traditional columns, may be employed in conjunction with the liquid-liquid extraction unit(s).

[0149] In one embodiment (not shown), the diluted liquid acrylate stream is fed to a liquid-liquid extraction column where the diluted liquid acrylate stream is contacted with an extraction agent, e.g., an organic solvent. The liquid-liquid extraction column extracts the acids, e.g., acrylic acid and acetic acid, from the diluted liquid acrylate stream. An aqueous phase comprising water, alkylenating agent, and some acetic acid exits the liquid-liquid extraction unit. Small amounts of acylic acid may also be present in the aqueous stream. The aqueous phase may be further treated and/or recycled. An organic phase comprising acrylic acid, acetic acid, and the extraction agent also exits the liquid-liquid extraction unit. The organic phase may also comprise water and formaldehyde. The acrylic acid may be separated from the organic phase and collected as product. The acetic acid may be separated then recycled and/or used elsewhere. The solvent may be recovered and recycled to the liquid-liquid extraction unit.

[0150] The inventive process further comprises the step of separating the intermediate acrylate product stream to form a finished acrylate product stream and a first finished acetic acid stream. The finished acrylate product stream comprises acrylate product(s) and the first finished acetic acid stream comprises acetic acid. The separation of the acrylate products from the intermediate

product stream to form the finished acrylate product may be referred to as the "acrylate product split."

[0151] Returning to FIG. 3, purified product stream 342 exits alkylenating agent split unit 332 and is directed to acrylate product split unit 334 for further separation, e.g., to further separate the acrylate products therefrom. Acrylate product split unit 334 may comprise any suitable separation device or combination of separation devices. For example, acrylate product split unit 334 may comprise at least one column, e.g., a standard distillation column, an extractive distillation column and/or an azeotropic distillation column. In other embodiments, acrylate product split unit 334 comprises a precipitation unit, e.g., a crystallizer and/or a chiller. Preferably, acrylate product split unit 334 comprises two standard distillation columns as shown in FIG. 3. In another embodiment, acrylate product split unit 334 comprises a liquid-liquid extraction unit. Of course, other suitable separation devices may be employed either alone or in combination with the devices mentioned herein.

[0152] In FIG. 3, acrylate product split unit 334 comprises second column 352 and third column 354. Acrylate product split unit 334 receives at least a portion of purified acrylic product stream in line 342 and separates same into finished acrylate product stream 356 and at least one acetic acid-containing stream. As such, acrylate product split unit 334 may yield the finished acrylate product.

[0153] As shown in FIG. 3, at least a portion of purified acrylic product stream in line 342 is directed to second column 352. Second column 352 separates the purified acrylic product stream to form second distillate, e.g., line 358, and second residue, which is the finished acrylate product stream, e.g., line 356. The distillate may be refluxed and the residue may be boiled up as shown. In some embodiments, at least a portion of residue 356 and/or distillate 358 may be recycled to line 315.

[0154] Stream 358 comprises acetic acid and some acrylic acid. The second column residue exits second column 352 in line 356 and comprises a significant portion of acrylate product. As such, stream 356 is a finished product stream. Exemplary compositional ranges for the distillate and residue of second column 352 are shown in Table 11. Components other than those listed in Table 11 may also be present in the residue and distillate.

TABLE 11
SECOND COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	0.1 to 40	1 to 30	5 to 30
Acetic Acid	60 to 99	70 to 90	75 to 85
Water	0.1 to 25	0.1 to 10	1 to 5
Alkylenating Agent	0.1 to 10	0.5 to 15	1 to 5
Propionic Acid	less than 10	0.001 to 5	0.001 to 1
Residue			
Acrylic Acid	at least 85	85 to 99.9	95 to 99.5
Acetic Acid	less than 15	0.1 to 10	0.1 to 5
Water	less than 1	less than 0.1	less than 0.01
Alkylenating Agent	less than 1	less than 0.1	less than 0.01
Propionic Acid	less than 1	less than 0.1	less than 0.01

[0155] Returning to FIG. 3, at least a portion of stream 358 is directed to third column 354. Third column 354 separates the at least a portion of stream 358 into a distillate in line 360 and a residue in line 362. The distillate may be refluxed and the residue may be boiled up as shown. The distillate comprises a major portion of acetic acid. In one embodiment, at least a portion of line 360 is returned, either directly or indirectly, to reactor 306. The third column residue exits third column 354 in line 362 and comprises acetic acid and some acrylic acid. At least a portion of line 362 may be returned to second column 352 for further separation. In one embodiment, at least a portion of line 362 is returned, either directly or indirectly, to reactor 306. In another embodiment, at least a portion of the acetic acid-containing stream in either or both of lines 360 and 362 may be directed to an ethanol production system that utilizes the hydrogenation of acetic acid to form the ethanol. In another embodiment, at least a portion of the acetic acid-containing stream in either or both of lines 360 and 362 may be directed to a vinyl acetate system that utilizes the reaction of ethylene, acetic acid, and oxygen form the vinyl acetate. In some embodiments, at least a portion of the acetic acid-containing stream in either or both of lines 360 and 362 may be recycled to line 315. In a preferred embodiment, at least a portion of line 360 is recycled to line 315. Exemplary compositional ranges for the distillate and residue of third column 354 are shown in Table 12. Components other than those listed in Table 12 may also be present in the residue and distillate.

TABLE 12
THIRD COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	0.01 to 10	0.05 to 5	0.1 to 1
Acetic Acid	50 to 99.9	70 to 99.5	80 to 99
Water	0.1 to 25	0.1 to 15	1 to 10
Alkylenating Agent	0.1 to 25	0.1 to 15	1 to 10
Propionic Acid	less than 1	less than 0.1	less than 0.01
Residue			
Acrylic Acid	5 to 50	15 to 40	20 to 35
Acetic Acid	50 to 95	60 to 80	65 to 75
Water	0.01 to 10	0.01 to 5	0.1 to 1
Alkylenating Agent	less than 1	0.001 to 1	0.01 to 1
Propionic Acid	less than 1	less than 0.1	less than 0.01

[0156] In cases where the acrylate product split unit comprises at least one column, the column(s) may be operated at suitable temperatures and pressures. In one embodiment, the temperature of the residue exiting the column(s) ranges from 90°C to 130°C, e.g., from 95°C to 120°C or from 100°C to 115°C. The temperature of the distillate exiting the column(s) preferably ranges from 60°C to 90°C, e.g., from 65°C to 85°C or from 70°C to 80°C. The pressure at which the column(s) are operated may range from 1 kPa to 300 kPa, e.g., from 10 kPa to 100 kPa or from 40 kPa to 80 kPa. In preferred embodiments, the pressure at which the column(s) are operated is kept at a low level e.g., less than 50 kPa, less than 27 kPa, or less than 20 kPa. In terms of lower limits, the column(s) may be operated at a pressures of at least 1 kPa, e.g., at least 3 kPa or at least 5 kPa. Without being bound by theory, it has surprisingly and unexpectedly been found that be maintaining a low pressure in the columns of acrylate product split unit 334 may inhibit and/or eliminate polymerization of the acrylate products, e.g., acrylic acid, which may contribute to fouling of the column(s).

[0157] It has also been found that, surprisingly and unexpectedly, maintaining the temperature of acrylic acid-containing streams fed to acrylate product split unit 334 at temperatures below 140°C, e.g., below 130°C or below 115°C, may inhibit and/or eliminate polymerization of acrylate products. In one embodiment, to maintain the liquid temperature at these temperatures, the pressure of the column(s) is maintained at or below the pressures mentioned above. In these cases, due to the lower pressures, the number of theoretical column trays is kept at a low level,

e.g., less than 10, less than 8, less than 7, or less than 5. As such, it has surprisingly and unexpectedly been found that multiple columns having fewer trays inhibit and/or eliminate acrylate product polymerization. In contrast, a column having a higher amount of trays, e.g., more than 10 trays or more than 15 trays, would suffer from fouling due to the polymerization of the acrylate products. Thus, in a preferred embodiment, the acrylic acid split is performed in at least two, e.g., at least three, columns, each of which have less than 10 trays, e.g. less than 7 trays. These columns each may operate at the lower pressures discussed above.

[0158] Returning to FIG. 3, alkylenating agent stream 340 exits alkylenating agent split unit 332 and is directed to drying unit 336 for further separation, e.g., to further separate the water therefrom. The separation of the formaldehyde from the water may be referred to as dehydration. Drying unit 336 may comprise any suitable separation device or combination of separation devices. For example, drying unit 338 may comprise at least one column, e.g., a standard distillation column, an extractive distillation column and/or an azeotropic distillation column. In other embodiments, drying unit 336 comprises a dryer and/or a molecular sieve unit. In a preferred embodiment, drying unit 336 comprises a liquid-liquid extraction unit. In one embodiment, drying unit 336 comprises a standard distillation column as shown in FIG. 3. Of course, other suitable separation devices may be employed either alone or in combination with the devices mentioned herein.

[0159] In FIG. 3, drying unit 336 comprises fourth column 370. Drying unit 336 receives at least a portion of alkylenating agent stream in line 340 and separates same into a fourth distillate comprising water, formaldehyde, and methanol in line 372 and a fourth residue comprising mostly water in line 374. The distillate may be refluxed and the residue may be boiled up as shown. In some preferred embodiments, at least a portion of fourth residue 374 is recycled to line 315. In one embodiment, at least a portion of line 372 is returned, either directly or indirectly, to reactor 306. Fourth column 370 may also receive water from the vaporizer in line 313. Line 313 may also comprise formaldehyde and methanol.

[0160] Exemplary compositional ranges for the distillate and residue of fourth column 370 are shown in Table 13. Components other than those listed in Table 13 may also be present in the residue and distillate.

TABLE 13
FOURTH COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	less than 1	less than 0.1	less than 0.01
Acetic Acid	less than 2	0.01 to 1	0.01 to 1
Water	20 to 90	30 to 80	40 to 70
Alkylenating Agent	10 to 70	20 to 60	30 to 50
Methanol	0.01 to 15	0.1 to 10	1 to 5
Residue			
Acrylic Acid	less than 1	0.001 to 1	0.01 to 1
Acetic Acid	less than 15	0.1 to 10	0.1 to 5
Water	at least 85	85 to 99.9	95 to 99.5
Alkylenating Agent	less than 1	0.001 to 1	0.1 to 1
Propionic Acid	less than 1	less than 0.1	less than 0.01

[0161] In cases where the drying unit comprises at least one column, the column(s) may be operated at suitable temperatures and pressures. In one embodiment, the temperature of the residue exiting the column(s) ranges from 90°C to 130°C, e.g., from 95°C to 120°C or from 100°C to 115°C. The temperature of the distillate exiting the column(s) preferably ranges from 60°C to 90°C, e.g., from 65°C to 85°C or from 70°C to 80°C. The pressure at which the column(s) are operated may range from 1 kPa to 500 kPa, e.g., from 25 kPa to 400 kPa or from 100 kPa to 300 kPa.

[0162] Returning to FIG. 3, alkylenating agent stream 372 exits drying unit 336 and is directed to methanol removal unit 338 for further separation, e.g., to further separate the methanol therefrom. Methanol removal unit 338 may comprise any suitable separation device or combination of separation devices. For example, methanol removal unit 338 may comprise at least one column, e.g., a standard distillation column, an extractive distillation column and/or an azeotropic distillation column. In one embodiment, methanol removal unit 338 comprises a liquid-liquid extraction unit. In a preferred embodiment, methanol removal unit 338 comprises a standard distillation column as shown in FIG. 3. Of course, other suitable separation devices may be employed either alone or in combination with the devices mentioned herein.

[0163] In FIG. 3, methanol removal unit 338 comprises fifth column 380. Methanol removal unit 338 receives at least a portion of line 372 and separates same into a fifth distillate comprising methanol and water in line 384 and a fifth residue comprising water and

formaldehyde in line 382. The distillate may be refluxed and the residue may be boiled up (not shown). In one embodiment, at least a portion of line 382 is returned, either directly or indirectly, to reactor 306. Fifth distillate 384 may be used to form formaldehyde.

[0164] Exemplary compositional ranges for the distillate and residue of fifth column 380 are shown in Table 14. Components other than those listed in Table 14 may also be present in the residue and distillate.

TABLE 14
FIFTH COLUMN

	Conc. (wt.%)	Conc. (wt.%)	Conc. (wt.%)
Distillate			
Acrylic Acid	less than 1	less than 0.1	less than 0.01
Acetic Acid	less than 1	less than 0.1	less than 0.01
Water	20 to 60	30 to 50	35 to 45
Alkylenating Agent	0.1 to 25	0.5 to 20	1 to 15
Methanol	20 to 70	30 to 60	40 to 50
Residue			
Acrylic Acid	less than 1	less than 0.1	less than 0.01
Acetic Acid	less than 15	0.1 to 10	0.1 to 5
Water	40 to 80	50 to 70	55 to 65
Alkylenating Agent	20 to 60	30 to 50	35 to 45
Methanol	less than 15	0.1 to 10	0.1 to 5

[0165] In cases where the methanol removal unit comprises at least one column, the column(s) may be operated at suitable temperatures and pressures. In one embodiment, the temperature of the residue exiting the column(s) ranges from 90°C to 130°C, e.g., from 95°C to 120°C or from 100°C to 115°C. The temperature of the distillate exiting the column(s) preferably ranges from 60°C to 90°C, e.g., from 65°C to 85°C or from 70°C to 80°C. The pressure at which the column(s) are operated may range from 1 kPa to 500 kPa, e.g., from 25 kPa to 400 kPa or from 100 kPa to 300 kPa.

EXAMPLES

Comparative Example A

[0166] A column feed comprised of 41.5 wt.% acetic acid, 33.2 wt.% acrylic acid, 9.2 wt.% formaldehyde and 16 wt.% water was fed to an alkylenating agent split column containing 40 trays. A small feed of polymerization inhibitor was fed to the top of the column to inhibit polymerization. Condenser pressure was 550 mm Hg and the reflux ratio was 5:1. The ratio of

distillate rate to feed rate, by mass, was 0.23:1. Table 15 below shows the percent of each component by its distribution between the distillate and the residue. Table 15 also shows the relative volatility of each component to acetic acid.

TABLE 15
COMPARATIVE EXAMPLE WITH NO LIQUID ACRYLATE STREAM DILUTION

Component	Distillate (% component)	Residue (% component)	Relative Volatility (to Acetic Acid)
Acrylic Acid	0.34	99.66	0.62
Acetic Acid	0.72	99.28	1
Water	87.92	12.10	1.31
Formaldehyde	45.37	54.63	0.8

Example 1

[0167] A column feed comprised of 49.3 wt.% acetic acid, 33.5 wt.% acrylic acid, 3.1 wt.% formaldehyde and 14.1 wt.% water was fed to an alkylenating agent split column containing 40 trays. The column feed of Example 1 was diluted with acetic acid and water. A small feed of polymerization inhibitor was fed to the top of the column to inhibit polymerization. Condenser pressure was 550 mm Hg and a the reflux ratio was 5:1. The ratio of distillate rate to feed rate, by mass, was 0.16:1. Table 16 below shows the percent of each component by its distribution between the distillate and the residue. Table 16 also shows the relative volatility of each component to acetic acid.

TABLE 16
DILUTED LIQUID ACRYLATE STREAM

Component	Distillate (% component)	Residue (% component)	Relative Volatility (to Acetic Acid)
Acrylic Acid	0.66	99.33	0.61
Acetic Acid	0.57	99.43	1
Water	65.24	34.76	1.32
Formaldehyde	64.41	35.59	1.15

[0168] As shown by Table 16, when the liquid acrylate stream is diluted with additional acetic acid, more formaldehyde is removed in the distillate, illustrating an increase in the volatility of formaldehyde. Further, the relative volatility of formaldehyde to acetic acid increases from 0.8 to 1.15.

[0169] While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference. In addition, it should be understood that aspects of the invention and portions of various embodiments and various features recited below and/or in the appended claims may be combined or interchanged either in whole or in part. In the foregoing descriptions of the various embodiments, those embodiments which refer to another embodiment may be appropriately combined with other embodiments as will be appreciated by one of skill in the art. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

We claim:

1. A process for producing an acrylate product, the process comprising the steps of:

reacting in a reactor a reaction mixture comprising alkanoic acid and an alkylenating agent to form a crude acrylate product;

removing inert and/or reactive gases from the crude acrylate product to form a liquid acrylate stream;

diluting the liquid acrylate stream with a diluent to form a diluted liquid acrylate stream; and

separating at least a portion of the diluted liquid acrylate stream to form a finished acrylate product.

2. The process of claim 1, wherein the diluent is selected from the group consisting of water, an alkanoic acid, acrylic acid, and combinations thereof.

3. The process of claim 2, wherein the diluted liquid acrylate stream comprises acrylate product and alkanoic acid, and further wherein the ratio of acrylate product to alkanoic acid is less than 0.25:1.

4. The process of claim 1, wherein the diluted liquid acrylate stream comprises from 30 wt% to 90 wt% alkanoic acid.

5. The process of claim 1, wherein the diluted liquid acrylate stream comprises less than 50 wt% acrylate product.

6. The process of claim 1, wherein the diluted liquid acrylate stream comprises less than 15 wt% alkylenating agent.

7. The process of claim 1, wherein the diluent comprises acetic acid.

8. The process of claim 1, wherein the relative volatility of the alkylenating agent to the acrylate product is at least 1:1.

9. The process of claim 1, wherein the separating step utilizes a separation unit other than a liquid-liquid extraction column.

10. The process of claim 1, wherein the separating further comprises:

separating at least a portion of the diluted liquid acrylate stream to form an alkylenating agent stream comprising at least 1 wt% alkylenating agent and an intermediate acrylate product stream comprising acrylate product and alkanoic acid.

11. The process of claim 10, wherein the separating further comprises:

separating the intermediate acrylate product to form the finished acrylate product comprising acrylate product and a finished alkanoic acid stream comprising alkanoic acid; and

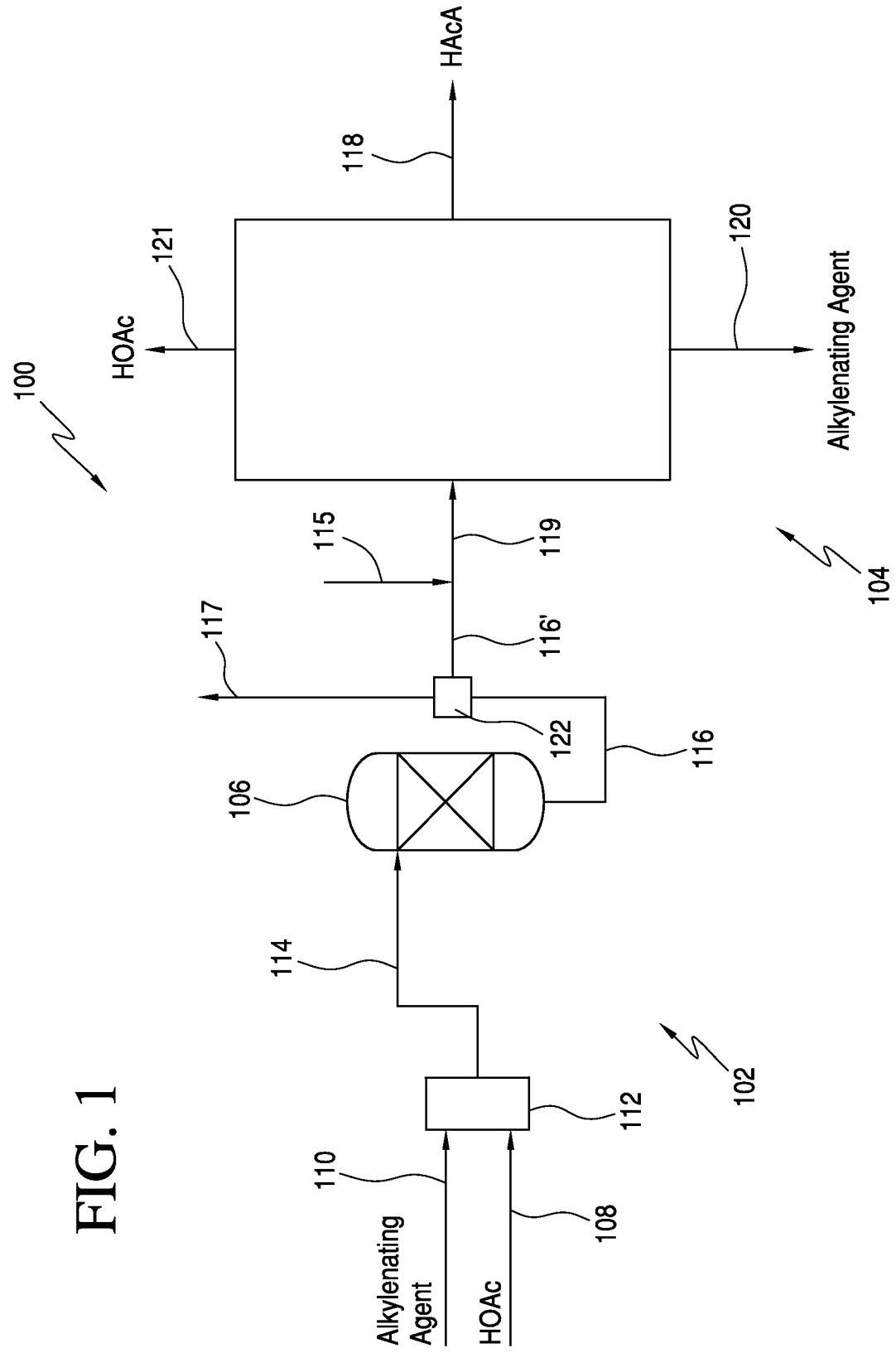
directing at least a portion of the finished alkanoic acid stream to the crude acrylate product.

12. The process of claim 11, wherein the finished alkanoic acid stream comprises less than 10 wt.% acrylate product.

13. The process of claim 1, wherein alkylenating agent conversion is at least 50 %.

14. The process of claim 1, wherein the alkanoic acid is acetic acid, the alkylenating agent is formaldehyde, and the diluent is acetic acid.

15. The process of claim 14, wherein the separating comprises separating acetic acid from the diluted liquid acrylate stream and recycling the separated acetic acid to the reactor; and further wherein the diluted liquid acrylate stream comprises from 30 to 75 wt.% acetic acid.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HOAc
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Alkylenating Agent
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Alkylenating Agent
HOAc

FIG. 1

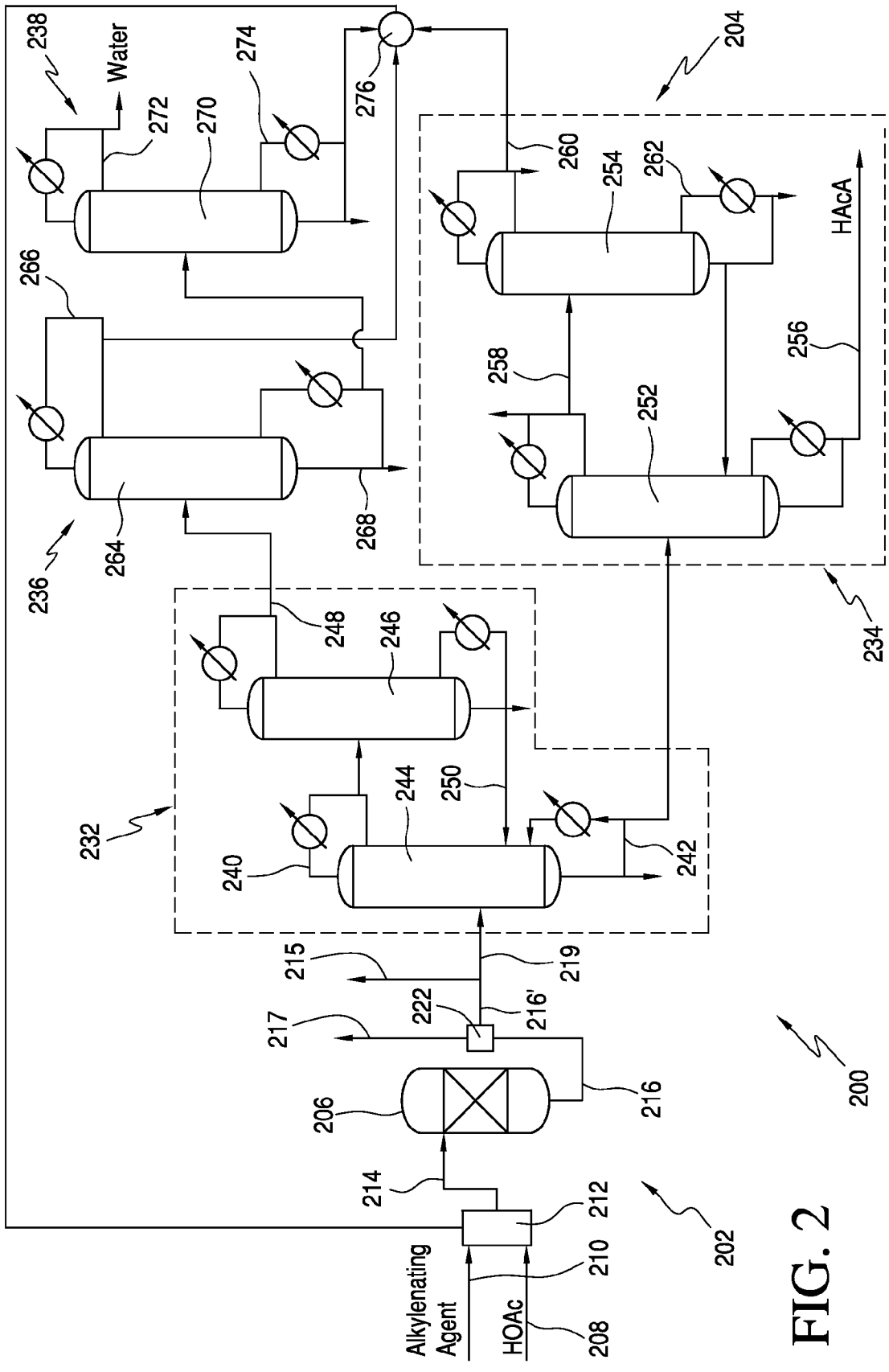
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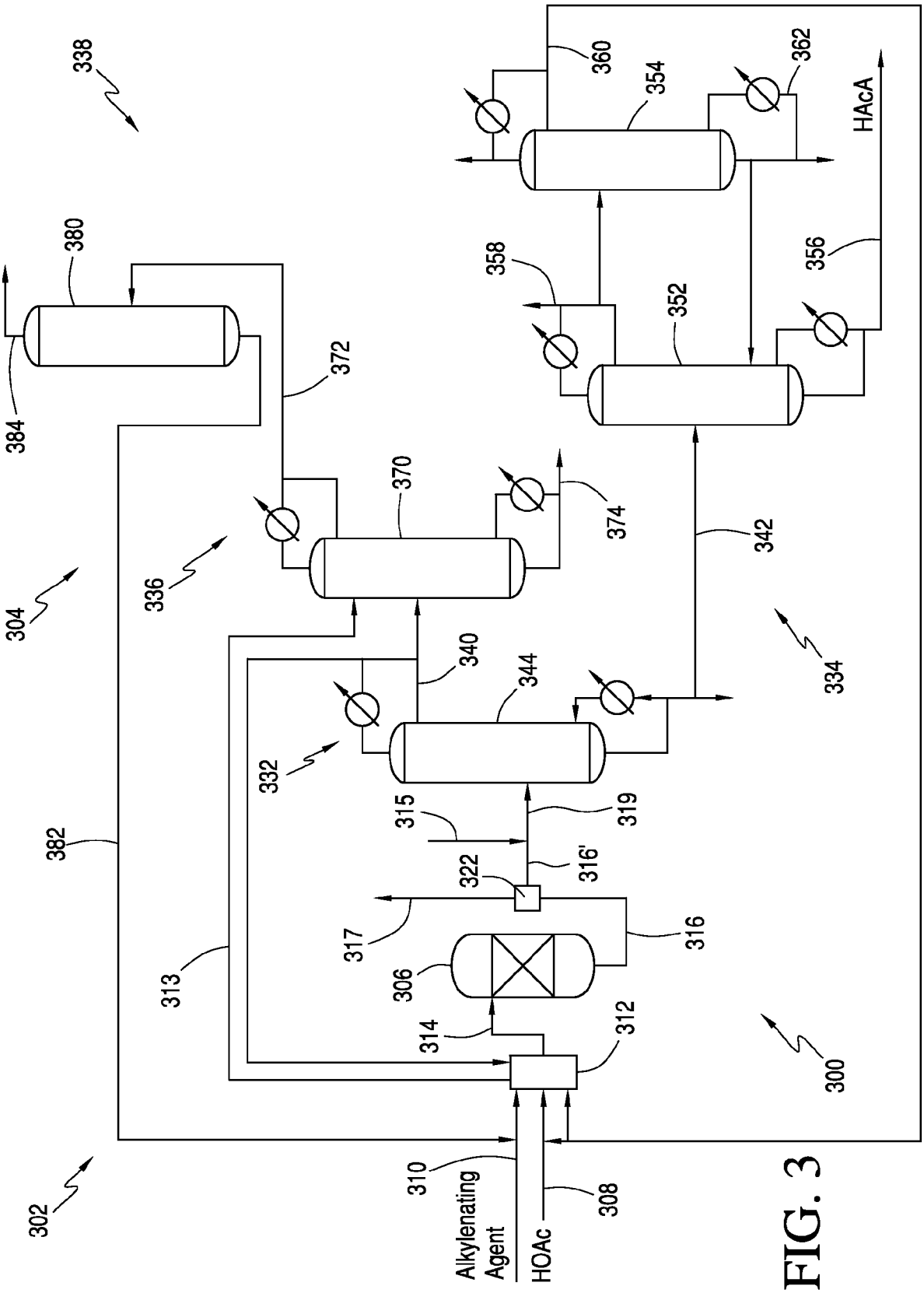
FIG. 2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Alkylenating Agent
HOAc

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/058441

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C67/317 C07C69/54 C07C51/42 C07C57/04
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MAMORU AI: "The production of methacrylic acidby the vapor-phase aldol condensation of propionic acid with formaldehyde", JOURNAL OF CATALYSIS, vol. 124, 1990, pages 293-296, XP002689804, page 293, right column, second paragraph, lines 1-7;; table 1 ----- -/--	1-15

[X] 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

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

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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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
22 January 2013	01/02/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Kleidernigg, Oliver

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MARORU AI ET.AL.: "Production of methacrylic acid by vapor-phase aldol condensation of propionic acid with formaldehyde over silica-supported metal phosphate catalysts", APPLIED CATALYSIS A: GENERAL, vol. 252, 2003, pages 185-191, XP002689805, page 185, right column, reaction scheme; page 186, right column paragraph 2.2 reaction procedures 1st and 2nd paragraph; Table 2; page 190, right column, paragraph 4 conclusions;	1-15
X	MAMORU AI: "Vapor-phase Aldol condensation of formaldehyde with acetic acid on V2O5-P2O5 catalysts", JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US, vol. 107, 1 January 1987 (1987-01-01), pages 201-208, XP002667283, ISSN: 0021-9517 cited in the application page 202, right column, paragraph results, lines 1-24;; figure 1	1-15