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(54) Title: PROCESS FOR THE MANUFACTURE OF AN ETHYLENE-DERIVED CHEMICAL OF INTEREST, IN PARTICULAR STYRENE, FROM RENEWABLY-SOURCED ETHANOL

(57) **Abstract:** A process for the manufacture of styrene comprises the steps of subjecting a feedstock comprising a renewably-sourced ethanol to dehydration to produce a renewably-sourced ethylene stream; and reacting the renewably-sourced ethylene stream with benzene in an alkylation reaction to produce ethylbenzene, and subjecting the ethylbenzene to a dehydrogenation reaction to produce styrene. The process provides a reaction scheme for renewably-sourced styrene.

WO 2024/089255 A1

Process for the Manufacture of an Ethylene-Derived Chemical of Interest, in Particular Styrene, from Renewably-Sourced Ethanol

Technical Background

The present invention relates to a process for the manufacture ethylene-derived chemicals, in particular styrene, from renewably-sourced ethanol.

Ethylene is a cornerstone of the modern petrochemical industries. Important ethylene derivatives (at the end of their respective chains) include (meth)acrylic acid, (meth)acrylic esters, isononanols, ethylhexanol, and ethylene glycols. One of the problems faced by the manufacture of chemicals and intermediates from ethylene is that the starting raw materials are from fossil fuels, such as natural gas or crude oil, which are non-renewable feedstocks. Steam cracking, which employs petroleum fractions and natural gas liquids as feedstocks, is the dominant method for large-scale ethylene production worldwide.

Lower olefins, such as isobutylene or propylene, are of significant interest for industrial and chemical applications. Isobutylene, also known as isobutene or 2-methylpropene, is a hydrocarbon of significant interest that is widely used as an intermediate in the production of industrially important products, including para-xylene, jet fuel blendstocks, gasoline oxygenates, isooctane, methacrolein, methyl methacrylate, and butyl rubber. Propylene is a hydrocarbon of significant interest that is widely used as an intermediate in the production of acrylic acid. Historically, lower olefins have been obtained through the catalytic or steam cracking of fossil fuel feedstocks.

Applicants have realized that the production of ethylene and ethylene derivatives compounds would benefit from the replacement of at least a part of the carbonaceous raw materials of fossil origin by renewable resources, such as carbonaceous matter derived from biomass. Of particular interest is the ethanol feedstock which is produced from renewable resources. Such renewably-sourced ethanol, also referred to as “bioethanol” or “hydrous fuel alcohol” can be prepared in large quantities from organic waste or biomass via fermentation. The different feedstocks for producing ethanol may be sucrose-containing feedstocks, e.g., sugarcane, starchy materials, e.g., corn, starch, wheat, cassava, lignocellulosic biomass, e.g., switchgrass, and/or agricultural waste. The purification or isolation of bioethanol is frequently carried out by complicated, multistage distillation.

Even after the purification processes, the advantage of bioethanol is frequently decreased by small amounts of impurities which it contains. Bioethanol impurities may include oxygen-containing organics, for example other alcohols such as isopropanol, n-propanol, and isobutanol, and/or aldehydes such as acetaldehyde. Bioethanol impurities may further include sulfur-containing impurities, such as inorganic sulfur compounds dialkyl sulfides, dialkyl sulfoxides, alkyl mercaptans, 3-methylthio-1-propanol, and/or sulfur-containing amino acids.

It would be desirable to integrate renewably-sourced ethanol into existing processes designed for the conversion of fossil-derived ethylene or its intermediates. However, some of the impurities may interfere with the downstream processes which use bioethanol as feedstock and which generate chemical products, especially when some of the downstream steps are catalytic conversions.

If efforts are not made to remove at least some of these impurities, the yield of desired intermediate and final products and efficacy of the overall process may be diminished.

US 2008/0312485 discloses a method for continuously producing propylene by dehydrating ethanol obtained from biomass to obtain ethylene and reacting ethylene with n-butene in a metathesis reaction. The n-butene is made by dimerization of ethylene which is obtained from biomass-derived ethanol [0033] and [0061].

WO 2010/066830 discloses the transformation of bioethanol to ethylene. The bioethanol is produced by fermentation of carbohydrates or from synthesis gas made by gasification of biomass. The ethylene is subsequently dimerized or oligomerized to, e.g., 1-butene and/or 1-hexene. The dimeric or oligomeric alpha-olefins are transformed into internal olefins that are subsequently subjected to metathesis with ethylene.

WO 2011/085223 discloses an integrated process to prepare renewable hydrocarbons. The process includes dehydrating renewable isobutanol to form a mixture of linear butenes and isobutene and dehydrating renewable ethanol to ethylene. Subsequently the butene mixture and the ethylene are reacted to form one or more renewable C_3-C_{16} olefins.

EP 3 067 340 A discloses a process comprising fermenting a renewable source of carbon for the production of a mixture of alcohols comprising ethanol, isopropanol and 1-butanol; joint dehydration of the alcohols to produce a mixture of olefins comprising chiefly ethylene, propylene and linear butenes, the linear butenes being a mixture of 1-butene and 2-butenes (cis- and trans-isomers), besides water and by-products; removal of water, oxygenated compounds and other by-products from the mixture of olefins, to generate a mixture of olefin comprising chiefly ethylene, propylene and linear butenes; and passing the mixture of olefins through an isomerization bed so that 1-butene is isomerized to 2-butene and subsequently passing the mixture of olefins comprising chiefly ethylene, propylene and 2-butenes through a metathesis bed, for reaction between ethylene and 2-butenes, generating additional propylene.

WO 2009/098268 discloses a process for the dehydration of an alcohol to make an olefin. The alcohol may be ethanol that can be obtained from carbohydrates. For this purpose a stream comprising the ethanol and an inert component is contacted with a catalyst to give ethylene. It is indicated that the ethylene can be used for dimerization to butene and then isomerization to isobutene, dimerization to 1-butene, which is isomerized to 2-butene and further converted by metathesis with ethylene to propylene, or conversion to ethylene oxide and glycol. Experimental details are provided only for ethanol dehydration. A similar process is disclosed in WO 2011/089235.

WO 2009/098269 discloses a process for conversion of ethanol that can be obtained from carbohydrates to propylene. The ethanol is dehydrated to ethylene which is reacted with olefins having four carbon atoms or more to give propylene. WO 2009/098267 discloses a similar process.

WO 2021/067294 discloses a process for simultaneously dehydrating, dimerizing and metathesizing a C_2-C_5 alcohol which can be from biobased processes in one reactor to produce a C_2-C_7 olefin.

WO 2009/070858 discloses an integrated process for the production of ethylene-butylene copolymers. The ethylene is obtained by dehydration of ethanol that is produced by the fermentation of sugars. One method of obtaining 1-butylene used for the polymerization is indicated to be dimerization of ethylene produced by dehydration of ethanol that is produced by the fermentation of sugars. No details as to the dimerization are given.

In embodiments, the invention seeks to advise a reaction scheme that provides renewably-sourced light olefins, such as ethylene, which partially or fully replace the light olefins output from a steam cracker. These light olefins are used as building blocks for producing a variety of chemicals of interest. It is desirable that the renewably-sourced light olefins can be blended or used interchangeably with a fossil-derived intermediate of the same chemical structure without necessitating adjustments in downstream processes. This includes that the starting olefins of all branches of the value chains, which historically have been served by the steam cracker output, can be supplied at the same time on a renewably-sourced basis. In this way, the greenhouse gases footprint and/or the carbon footprint for the production of a chemical of interest is at least reduced.

Detailed Description of the Invention

To this effect, the present invention relates to a process for the manufacture of a chemical of interest selected from ethylene-derived chemicals other than C_{3-4}-olefins, said process comprising the steps of:

a) subjecting a feedstock comprising a renewably-sourced ethanol to dehydration to produce a renewably-sourced ethylene stream; and

b) subjecting the renewably-sourced ethylene to a chemical conversion or sequence of chemical conversions to obtain the chemical of interest.

In particular, the present invention relates to a process for the manufacture of styrene, said process comprising the steps of:

a) subjecting a feedstock comprising a renewably-sourced ethanol to dehydration to produce a renewably-sourced ethylene stream; and

b) reacting the renewably-sourced ethylene stream with benzene in an alkylation reaction to produce ethylbenzene, and subjecting the ethylbenzene to a dehydrogenation reaction to produce styrene.

The process of the invention is preferably a continuous process in the sense that at least one of steps a) and b) is carried out continuously. In a still more preferred embodiment all steps of a reaction route leading to a chemical of interest are carried out continuously. This does not preclude the presence of buffer volumes between subsequent reaction steps in a reaction route.

The present invention is based on the idea of eliminating impurities that are inherently present in renewably-sourced ethanol during the ethylene manufacturing process itself.

Hence, the renewably-sourced ethylene can be blended or used interchangeably with a fossil-derived ethylene without necessitating adjustments in downstream processes.

It is envisaged that the renewably-sourced ethylene involved in the process according to the invention may be blended with complementary ethylene from other sources. This can ensure the efficient utilization of downstream processes, e.g., for transitional periods when supply of renewably-sourced ethylene is limited. The complementary ethylene may be fossil-based, partially renewably-sourced or renewably-sourced by another production route.

Hence in an embodiment, the process comprises blending the renewably-sourced ethylene with complementary ethylene prior to step b), the complementary ethylene not being obtained from renewably-sourced ethanol in accordance with step a). Examples for complementary ethylenes are ethylenes obtained by steam cracking of fossil based feeds, like naphtha, natural gas or crude oil.

In another aspect, the invention also relates to a process for enhancing the environmental sustainability of styrene by blending or replacing a fossil-derived ethylene with a renewably-sourced ethylene to obtain a sustainability-enhanced ethylene and reacting the sustainability-enhanced ethylene with benzene in an alkylation reaction to produce ethylbenzene, and subjecting the ethylbenzene to a dehydrogenation reaction to produce styrene, wherein the renewably-sourced ethylene is obtained by subjecting a feedstock comprising a renewably-sourced ethanol to dehydration to produce the renewably-sourced ethylene stream.

The key advantage of the process according to the present invention is that it can be easily integrated into an existing production site in which one or more chemicals of interest are manufactured based on a fossil feedstock, in particular naphtha. This means that fossil-based ethylene can be fully or partially substituted by renewably-sourced ethylene. Hereby, one obtains a respective chemical of interest, the carbon atoms of which are fully or partially based on a renewable-sourced carbon (so-called “green” carbon).

Further benefits occur from the reduction of carbon dioxide emissions. The chemical conversions involved in a reaction route leading to an individual chemical of interest are usually less than 100% selective. The yield losses manifest themselves in the generation of by-products that vary depending on the type of reaction involved. Oxidation reactions of a substrate to a desired product, for example, are almost invariably accompanied to a certain extent by an over-oxidation of the substrate to form carbon oxides, in particular carbon dioxide. By a full or partial replacement of fossil ethylene and by their renewably-sourced counterparts, the fossil-based carbon dioxide emissions of the entire production site can be reduced because respective emissions resulting from yield losses along the value chain are at least partially based on green carbon. The resulting carbon dioxide emissions therefore do not contribute to the green house emission of the production site. For example, in the production of ethylene oxide (as further described below) carbon dioxide is formed due to full oxidation of ethylene. Using a renewably-sourced ethylene as obtained by the process according to the present invention therefore prevents the formation of fossil-based carbon dioxide emissions resulting from such productions.

In addition, in non-oxidative reactions the various species present may undergo a host of side reactions, which generate color forming species, oligomers, and various decomposition products or the like. These are generally removed during work-up, e.g., by distillation, yielding light boiler and/or high boiler fractions in addition to the desired product. The light boiler or high boiler fractions are conventionally used for their calorific value, i.e. combusted as fuel, or exploited as hydrocarbon source, e.g. as steam cracker feed. It should be appreciated that full or partial replacement of fossil ethylene byits renewably-sourced counterpart at the beginning of the processing chain reduces the emission of fossil-based carbon dioxide resulting from the combustion of downstream side-products.

Hence, it is envisaged that direct and indirect benefits are associated with the process of the invention with regard to any chemical of interest that is manufactured via the process according to the present invention.

The expressions “renewable“ or “renewably-sourced“ in relation to a chemical compound are used synonymously and mean a chemical compound comprising a quantity of renewable carbon, i.e., having a reduced or no carbon content of fossil origin. Renewable carbon entails all carbon sources that avoid or substitute the use of any additional fossil carbon from the geosphere. Renewable carbon can come from the biosphere, atmosphere or technosphere – but not from the geosphere. Thus, the expression “renewable“ or “renewably-sourced“ includes, in particular, biomass-derived chemical compounds. It also includes compounds derived from waste such as polymer residues, or from waste streams of chemical production processes.

The expression “chemical of interest” collectively refers to any desired compound appearing in a value chain starting out from and including ethylene. Thus, the expression includes any intermediates and final products. In certain cases, a chemical compound can be an intermediate and final product at the same time. For example, styrene can be the final product of a value chain and yet can be an intermediate when it is further processed, if desired.

All patent and literature documents addressed in the following are incorporated herein by reference in their entirety.

Bioethanol is a preferred form of renewably-sourced ethanol, although the scope of the invention is not limited to the use of bioethanol.

In the present invention, bioethanol refers to the ethanol obtained from a biomass feedstock, such as plant or non-crop feedstock containing a carbon source that is convertible to ethanol, for example by microbial metabolism. Typical carbon source examples are starch, sugars like pentoses or hexoses, such as glucose, fructose, sucrose, xylose, arabinose, or degradation products of plants, hydrolysis products of cellulose or juice of sugar canes, beet and the like containing large amounts of the above components.

Biomass feedstock can originate from several sources. Bioethanol production may be based on food crop feedstocks such as corn and sugar cane, sugarcane bagasse, cassava (first generation biofeedstock).

Another source of biomass feedstock is lignocellulosic materials from agricultural crops (second-generation biofeedstock). Potential feedstocks include agricultural residue by-products such as rice, straw (such as wheat, oat and barley straw), rice husk, and corn stover. Biomass feedstock may also be waste material from the forest products industry (wood waste) and saw dust or produced on purpose as an ethanol crop. Switchgrass and napier grass may be used as on-purpose crops for conversion to ethanol.

The first-generation bioethanol is produced in four basic steps:

(1) Enzymatic saccharification or hydrolysis of starch into sugars

(2) Microbial fermentation of sugars

(3) Purification by distillation to give hydrous ethanol

(4) Dehydration (water removal) to produce anhydrous ethanol

Second-generation feedstocks are considered as renewable and sustainable carbon source. Pretreatment of this feedstock is an essential prerequisite before it is subjected to enzymatic hydrolysis, fermentation, distillation, and dehydration. Pretreatment involves milling and exposure to acid and heat to reduce the size of the plant fibers and hydrolyze a portion of the material to yield fermentable sugars. Saccharification utilizes enzymes to hydrolyze another portion to sugar. Finally, fermentation by bioengineered microorganisms converts the various sugars (pentoses and hexoses) to ethanol. The production of bioethanol is well-known and carried out on an industrial large scale.

Renewably-sourced ethanol can also be obtained from carbon-containing waste materials like waste products from the chemical industry, garbage and sewage sludge. The production of ethanol from waste materials can be done by gasification to syngas and catalytic conversion thereof the ethanol, see for example Recent Advances in Thermo-Chemical Conversion of Biomass, 2015, Pages 213-250, https://doi.org/10.1016/B978-0-444-63289-0.00008-9, and Nat Commun 11, 827 (2020), https://doi.org/10.1038/s41467-020-14672-8.

Dehydration of Renewably-Sourced Ethanol

As a first step, the invention involves the dehydration of renewably-sourced ethanol. The production of ethylene by catalytic dehydration of ethanol is a well-known process. The reaction is commonly carried out at 300 to 400 °C and moderate pressure in the presence of a catalyst. Catalytic effects are reviewed in Ind & Eng Chem Research, 52, 28, 9505-9514 (2013), Materials 6, 101-115 (2013) and ACS Omega, 2, 4287-4296 (2017). Examples for catalysts are activated alumina or silica, phosphoric acid impregnated on coke, heteropoly acids (HPA salts), silica-alumina, molecular sieves such as zeoliths of the ZSM-5 type or SAPO-11 type, other zeolites or modified zeolites of various molecular structures with zeoliths and HPA salts being preferred.

Ethanol dehydration is, for example described in WO 2009/098268, WO 2010/066830, WO 2009/070858 and the prior art discussed therein, WO 2011/085223 and the prior art discussed therein, US 4,234,752, US 4,396,789, US 4,529,827 and WO 2004/078336.

The ethanol dehydration reaction is in general carried out in the vapor phase in contact with a heterogeneous catalyst bed using either fixed bed or fluidized bed reactors. For fixed bed reactors, the operation can be either isothermal (with external heating system) or adiabatic (in the presence of a heat carrying fluid). The feedstock is vaporized and heated to the desired reaction temperature; the temperature drops as the reaction proceeds in the reactor. Multiple reactor beds are usually used in series to maintain the temperature drop in each bed to a manageable range. The cooled effluent from each bed is further heated to bring it to the desired inlet temperature of the subsequent beds. Moreover, a portion of the water is recirculated along with fresh and unreacted ethanol. The presence of water helps in moderating the temperature decrease in each bed.

Prior to dehydration, the renewably-sourced ethanol feedstock may be sent to a pretreatment section to remove mineral contaminants, which would otherwise be detrimental to the downstream catalytic reaction. The pretreatment may involve contacting the renewably-sourced ethanol feedstock with cation and/or anion exchange resins. After a certain period of operation, the resins may be regenerated by passing a regenerant solution through the resin bed(s) to restore their ion exchange capacity. Two sets of beds are preferably operated in parallel to maintain continuous operation. One set of resin beds is suitably regenerated while the other set is being used for pretreatment.

In the isothermal design, the catalyst is placed inside the tubes of multitubular fixed-bed reactors which arranged vertically and surrounded by a shell (tube and shell design). A heat transfer medium, such as molten salts or oil, is circulated inside the shell to provide the required heat. Baffles may be provided on the shell side to facilitate heat transfer. The cooled heating medium is heated externally and is recirculated. The temperature drop on the process side can be reduced as compared to the adiabatic reactor. A better control on the temperature results in increased selectivity for the ethylene formation and reduction in the amount of undesireable by-products. The temperature is maintained at approximately constant levels within the range of 300° to 350°C. Ethanol conversion is between 98 and 99%, and the selectivity to ethylene is between 94 and 97 mol%. Because of the rate of coke deposition, the catalyst must be regenerated frequently. Depending on the type of catalyst used, the cycle life is between 3 weeks and 4 months, followed by regeneration, for example for 3 days.

In the adiabatic design, the endothermic heat of reaction is supplied by a preheated inert diluent such as steam. Three fixed-bed reactors may typically be used, with intermediate furnaces to reheat the ethanol/ steam mixed feed stream to each reactor. Feeding steam with ethanol results in less coke formation, longer catalyst activity, and higher yields.

A further process is a fluidized-bed process. The fluidized-bed system offers excellent temperature control in the reactor, thereby minimizing by-product formation. The heat distribution rate of the fluidized bed operation approaches isothermal conditions. The endothermic heat of reaction is supplied by the hot recycled silica-alumina catalyst returning from the catalyst regenerator. Thus, external heating of the reactor is not necessary.

After dehydration, the reaction mixture is subjected to a separation step. The general separation scheme consists of quickly cooling the reaction gas, for example in a water quench tower, which separates most of the by-product water and the unreacted ethanol from ethylene and other light components which, for example exit from the top of the quench tower. In one type of separation scheme, the water-washed ethylene stream is immediately caustic-washed, for example in a column, to remove traces of CO_2. The gaseous stream may enter a compressor directly or pass to a surge gas holder first and then to a gas compressor. After compression, the gas is cooled with refrigeration and then passed through an adsorber with, for example activated carbon, to remove traces of heavy components, (e.g., C4s), if they are present. The adsorber is followed by a desiccant drying and dust filtering step before the ethylene product leaves the plant. This separation scheme produces 99%+ purity ethylene. If desired, the ethylene is further purified by caustic washing and desiccant-drying, and fractionated in a low-temperature column to obtain the final product.

Several commercial processes are currently in operation, developed by Braskem, Chematur, British Petroleum (BP), and Axens together with Total and IFPEN. The processes differ, e.g., in their process conditions, catalysts and adopted heat integration scheme. The process by BP (now Technip) is called Hummingbird. In this process, a heteropoly acid is used as catalyst, and the reactor operates at 160 to 270 °C and 1 to 45 bar. The unreacted ethanol in recirculated to the reactor. The process developed by Axens is called Atol. Two fixed bed adiabatic reactors, operating at 400 to 500 °C, are used. Chematur’s process operates with four adiabatic tubular reactors. Syndol catalysts, with the main components of Al_2O_3-MgO/SiO_2, are employed in this process that was developed by American Halcon Scientific Design, Inc. in the 1980s. In the Braskem process, the adiabatic reactor feed is diluted with steam to a large extent. In such a process, the reactor operates at 180 to 600 °C, preferably 300 to 500 °C, and at 1.9 to 19.6 bar. An alumina or silica-alumina catalyst is used. The Braskem process is described in more detail in US 4,232,179. A process control in accordance with the Braskem process is particularly preferred.

Alkylation of Ethylene with Benzene

Reacting the renewably-sourced ethylene stream with benzene in an alkylation reaction produces ethylbenzene, and subjecting the ethylbenzene to a dehydrogenation reaction produces styrene.

Benzene can be alkylated with ethane preferably in liquid phase to produce ethylbenzene. In general, the alkylation is carried out at a temperature of 80 to 130 °C and in the presence of a Lewis acid catalyst such as $AlCl_3$, $AlBr_3$, $FeCl_3$, $ZrCl_4$, and BF_3 with $AlCl_3$ being preferred. Ethyl chloride or hydrogen chloride may be used as a catalyst promoter. Further details can be taken from Ullmann's Encyclopedia of Industrial Chemistry, 5th ed., vol. A10, 35-40, 1987.

Dehydrogenation of Ethylbenzene to Styrene

To produce styrene the obtained ethylbenzene is dehydrogenated in the vapor phase with steam over a catalyst comprising iron oxide. The dehydrogenation can be carried out adiabatically or isothermally. Further details can be taken from Ullmann's Encyclopedia of Industrial Chemistry, 6th ed., vol. 34, 386-390, 2003.

Additional Embodiments

The present invention also relates to processes for the manufacture of a chemical of interest selected from ethylene-derived chemicals other than C_{3-4}-olefins according to the following embodiments.

1. Process for the manufacture of a chemical of interest selected from ethylene-derived chemicals other than C_{3-4}-olefins, said process comprising the steps of:
   a) subjecting a feedstock comprising a renewably-sourced ethanol to dehydration to produce a renewably-sourced ethylene stream; and
   b) subjecting the renewably-sourced ethylene to a chemical conversion or sequence of chemical conversions to obtain the chemical of interest.

2. Process according to embodiment 1, wherein step b) comprises hydroformylation of the renewably-sourced ethylene to produce propionaldehyde.

3. Process according to embodiment 2, wherein step b) further comprises reaction of the propionaldehyde with formaldehyde to produce methacrolein, and optionally comprises oxidation of the methacrolein to produce methacrylic acid.

4. Process according to embodiment 3, wherein step b) further comprises an esterification reaction of the methacrylic acid to produce a methacrylic ester.

5. Process according to embodiment 1, wherein step b) comprises an epoxidation reaction of the renewably-sourced ethylene to produce ethylene oxide, and
    - optionally, a hydrolysis reaction of the ethylene oxide to produce ethylene glycol and/or ethylene glycol ethers, or
    - optionally, an amination reaction of the ethylene oxide to produce ethanolamines and/or ethylene amines.

6. Process according to embodiment 5, wherein the epoxidation reaction progresses under formation of CO_x as a side product, and the process further comprises subjecting said CO_x to hydrogenation to produce at least one of synthesis gas, methanol, formaldehyde and formic acid.

Hydroformylation of Ethylene to Produce Propionaldehyde

In an embodiment, step b) comprises hydroformylation of the renewably-sourced ethylene to produce propionaldehyde.

Hydroformylation or the oxo process is an important large-scale industrial process for preparing aldehydes from olefins, carbon monoxide and hydrogen. These aldehydes can optionally be hydrogenated with hydrogen in the same operation or subsequently in a separate hydrogenation step, to produce the corresponding alcohols. In general, hydroformylation is carried out in the presence of catalysts which are homogeneously dissolved in the reaction medium. Catalysts used are generally the carbonyl complexes of metals of transition group VIII, in particular Co, Rh, Ir, Pd, Pt or Ru, which may be unmodified or modified with, for example, amine-containing or phosphine-containing ligands. A summarizing account of the processes practiced on a large scale in industry is found in J. Falbe, “New Syntheses with Carbon Monoxide”, Springer Verlag 1980, p. 162 ff., US 3,527,809; 3,917,661; 4,148,830; 4,742,178, 4,769,984; 4,885,401; 6,049,011.

Ethylene is preferably hydroformylated using ligand-modified rhodium carbonyls as the catalyst. Hydroformylation of ethylene can be carried out at temperatures in the range of 50 °C to 200 °C, preferably 60 °C to 150 °C, and more preferably 70 °C to 120 °C.

In one embodiment, the hydroformylation reaction is conducted at a low pressure, e.g., a pressure in the range of 0.05 to 50 MPa (absolute), and preferably in the range of about 0.1 MPa to 30 MPa, most preferably at a pressure below 5 MPa. Desirably, the partial pressure of carbon monoxide is not greater than 50% of the total pressure.

The proportions of carbon monoxide, hydrogen, and ethylene in the hydroformylation reaction medium can be selected within a wide range. In some embodiments, based on the total amount of CO, hydrogen, and ethylene, CO is from about 1 to 50 mol-%, preferably about 1 to 35 mol-%; H_2 is from about 1 to 98 mol-%, preferably about 10 to 90 mol-%; and ethylene is from about 0.1 to 35 mol-%, preferably about 1 to 35 mol-%.

The hydroformylation reaction preferably takes place in the presence of both liquid and gas phases. The reactants generally are in the gas phase. The catalyst typically is in the liquid phase. Because the reactants are gaseous compounds, a high contact surface area between the gas and liquid phases is desirable to enhance good mass transfer. A high contact surface area between the catalyst solution and the gas phase may be provided in any suitable manner. In a batch process, the batch contents are thoroughly mixed during the course of the reaction. In a continuous operation the reactor feed gas can be contacted with the catalyst solution in, for example, a continuous-flow stirred autoclave where the gas is introduced and dispersed at the bottom of the vessel, preferably through a perforated inlet (e.g., a sparger). High contact between the catalyst and the gas feed may also be provided by dispersing the solution of the Rh catalyst on a high surface area support, a technique well known in the art as supported liquid phase catalysis, or providing the Rh as part of a permeable gel.

The reaction may be conducted either in a batch mode or, preferably, on a continuous basis. One or more reactors may be used in continuous modes to carry out the reaction in one or more stages.

The ratio of H_2 to CO in the syngas used for hydroformylation is desirably in the range from 1.1:1 to 1.01:1, preferably 1.06:1 to 1.02:1. Often, syngas may be made or otherwise initially provided in a manner such that the ratio of hydrogen to CO is much higher than this. The excess hydrogen can be separated and used in other reaction stages as desired. For example, the excess hydrogen may be used to reduce propionaldehyde to propanol. In some modes of practice, syngas in the practice of the present invention is anhydrous.

Reaction of Propionaldehyde with Formaldehyde to Produce Methacrolein

The propionaldehyde obtained by hydroformylation of ethylene may be subjected to an aldol condensation as described below. Thus, in one embodiment, step b) further comprises reaction of the propionaldehyde with formaldehyde to produce methacrolein, and optionally comprises oxidation of the methacrolein to produce methacrylic acid.

An aldol condensation is a well-known condensation reaction in which an enol or an enolate ion reacts with a carbonyl compound to form a β-hydroxyaldehyde or β-hydroxyketone (an aldol reaction) in the presence of an acid or base catalyst, followed by dehydration to give a conjugated enone and hydrogenation to the corresponding alcohol. In the present case propionaldehyde is reacted with formaldehyde in a cross-aldol condensation to obtain methacrolein.

Aldol condensations can occur under a variety of conditions under weak acidic or strong basic conditions and in the presence of various catalysts. In the present case a catalyst system comprising a secondary amine, preferably a di-C_1-C_6-alkylamine or a 4-, 5- or 6-membered cyclic mono or diamine, and an organic acid with up to 10 carbon atoms, preferably a mono or dicarboxylic acid, is preferably used. Examples for amines are dimethylamine, diethylamine, methyl ethyl amine, ethyl butyl amine, di-n-butylamine, di-2-ethylhexylamine, diisooctylamine, diphenylamine, dicyclohexylamine, piperidine, piperazine or morpholine or a combination thereof. Examples for organic acids are formic, acetic, propionic, malic, malonic, glutaric, tartaric, adipic, succinic, hydroxy succinic, maleic, 2-ethylhexanoic or salicylic acid or combinations thereof.

The molar ratio of formaldehyde to propionaldehyde is preferably in the range of 1:1 to 1.5:1. The secondary amine is preferably used in a molar ratio of 0.005:1 to 0.1:1 to the propionaldehyde. The organic acid may be used in a molar ratio of 0.002:1 to 0.05:1 to propionaldehyde.

The reaction temperature may be in the range from 70 °C to 120 °C, preferably 80 °C to 100 °C, and the pressure may be from 100 kPa to 300 kPa, preferably 150 to 250 kPa.

Oxidation of Methacrolein to Produce Methacrylic Acid

In one embodiment, the methacrolein obtained by the aldol condensation may be further reacted in an oxidation reaction to methacrylic acid.

The oxidation of methacrolein is typically carried out in the gas phase. In this case, the oxidizing agent used is preferably a gas mixture containing oxygen and steam, which is passed over the catalyst, generally in the form of a fixed catalyst bed.

Suitable catalysts include multi-metal oxide catalysts comprising Mo and P, and optionally further at least one element selected from Cu, Cs, Ca, As, Sb, Nb, V, W, Fe, Mn, Sn and Cr.

The process is generally carried out under pressures of from 1 to 5 bar, advantageously from 1 to 2.5 bar. In the process, the residence time of the methacrolein-containing gas mixtures is, based on standard conditions, generally 0.5 to 5 seconds or 1 to 3 seconds. The temperature is preferably in the range of 200 to 340 °C, especially from 220 to 320 °C.

In addition to oxygen, methacrolein and steam the reaction gases in general contain inert gases, especially nitrogen; the oxygen is in general introduced as air but can also be employed as pure oxygen. Moreover, the reaction gas generally contains carbon oxides, especially if the reaction exit gas remaining after isolation of the methacrylic acid formed is recycled as a diluent, together with unconverted methacrolein, to the oxidation reaction.

In the reaction gas, the molar ratio of methacrolein : oxygen : water : inert gas is generally 1:1 - 6:1 - 20:4 - 50, preferably 1:1.5 - 4:2 - 10:6 - 30. The methacrylic acid can be isolated from the hot reaction exit gases in a conventional manner, generally by chilling with water.

Esterification of Methacrylic Acid to Produce a Methacrylic Ester

In an embodiment, step c) further comprises an esterification reaction of the methacrylic acid to produce a methacrylic ester.

(Meth)acrylic esters are generally known and are important, for example, as reactive monoethylenically unsaturated monomers for the preparation of aqueous polymer dispersions by the free radical aqueous emulsion polymerization method, which dispersions are used, for example, as adhesives.

The methacrylic acid can be esterified in a conventional manner to produce the desired methacrylic acid ester using the corresponding alkanol such as methanol, ethanol, n-propanol, isopropanol, n-butanol and 2-ethylhexanol.

Processes for the preparation of alkyl methacrylates by reacting methacrylic acid with alkanols in the homogeneous liquid phase at elevated temperatures and in the presence of catalysts are equilibrium reactions in which the conversion of the methacrylic acid and of the alkanol to the corresponding ester is limited by the equilibrium constant. Consequently, for an economical procedure, the unconverted starting materials have to be separated from the resulting ester and recycled to the reaction zone.

Conveniently, the reaction zone may consist of a cascade of reaction regions, connected in series, and the discharge stream of one reaction region forms a feed stream of a subsequent reaction region and the concentration of the esterification catalyst increases along the reaction cascade. Methacrylic acid, the alkanol and the catalyst are fed continuously to the reaction zone. An azeotropic mixture comprising the alkyl (meth)acrylate, water and optionally starting alkanol is separated off by rectification via the top of a rectification zone mounted on the reaction zone. The azeotropic mixture is separated into an organic phase containing the alkyl (meth)acrylate and an aqueous phase, with a part of the organic phase being recycled to the reaction zone. The alkyl (meth)acrylate is isolated from the excess organic phase. The latter is usually carried out by separation steps involving rectification (cf. for example DE 19536178).

The temperature in the reaction zone depends on the type of alcohol used and is suitably in the range of 70 to 160 °C, preferably 100 to 140 °C. The total residence time of the reactants in the reaction zone is as a rule from 0.25 to 15 h, frequently from 1 to 7 h, or from 2 to 5 h.

Suitable acidic esterification catalysts include acidic ion exchange resins and strong mineral acids, e.g. sulfuric acid, or organic sulfonic acids, such as methanesulfonic acid, benzenesulfonic acid, dodecanesulfonic acid or para-toluenesulfonic acid, or a mixture of some or all of the abovementioned acids. Sulfuric acid is particularly suitable for carrying out the novel process. This applies in particular to the preparation of n-butyl acrylate.

The content of acidic esterification catalyst in the reaction zone is expediently from 0.1 to 20 wt.-%, frequently from 0.5 to 5 wt.-%, based on the reaction mixture contained therein.

To prevent undesired formation of polymer initiated by free radicals, a polymerization inhibitor is typically used during esterification. Examples of suitable polymerization inhibitors are hydroquinone, 4-methoxyphenol, and phenothiazine, which may be used singly or in admixture with each other. It is usual to add from about 0.01 to 0.1 wt.-% of polymerization inhibitor to the esterification mixture and mixtures containing the methacrylic ester.

Epoxidation of Ethylene

In an embodiment, step b) comprises an epoxidation reaction of the renewably-sourced ethylene to produce ethylene oxide, and

- optionally, a hydrolysis reaction of the ethylene oxide to produce ethylene glycol, or
- optionally, an amination reaction of the ethylene oxide to produce ethanolamines and/or ethylene amines.

Ethylene oxide is produced in large volumes and is primarily used as an intermediate in the production of several industrial chemicals. Suitable epoxidation catalysts are generally obtained by depositing metallic silver on a support. Highly selective silver-based epoxidation catalysts have been developed, which comprise, in addition to silver as the active component, promoting species for improving the catalytic properties of the catalyst, as described in, e.g., WO 2007/122090 A2 and WO 2010/123856 A1. Examples of promoting species include alkali metal compounds and/or alkaline earth metal compounds, as well as transition metals such as rhenium, tungsten or molybdenum.

Suitable catalysts typically comprise 20 to 35 % or 25 to 45 wt.-% of silver, relative to the weight of the catalyst.

As support material, it is possible to use various porous refractory materials such as activated carbon, titania, zirconia, silica, alumina or ceramic compositions or mixtures of these materials. Preferably, the refractory support is an aluminium oxide support. The supports preferably has a BET surface area of 0.5 to 3.0 m^2/g.

A suitable catalyst may be obtained by

i) impregnating a refractory support with a silver impregnation solution, preferably under reduced pressure; and optionally subjecting the impregnated refractory support to drying; and

ii) subjecting the impregnated refractory support to a calcination process;

wherein steps i) and ii) are optionally repeated.

The epoxidation of ethylene preferably comprises reacting ethylene and oxygen in the presence of an epoxidation catalyst as described above. The epoxidation can be carried out by all processes known to those skilled in the art. It is possible to use all reactors which can be used in the ethylene oxide production processes of the prior art; for example externally cooled shell-and-tube reactors (cf. Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, vol. A-10, pp. 117-135, 123-125, VCH-Verlagsgesellschaft, Weinheim 1987) or reactors having a loose catalyst bed and cooling tubes, for example the reactors described in DE 34 14 717 A1, EP 0 082 609 A1 and EP 0 339 748 A2.

The epoxidation is preferably carried out in at least one tube reactor, preferably in a shell-and-tube reactor. On a commercial scale, ethylene epoxidation is preferably carried out in a multi-tube reactor that contains several thousand tubes. The catalyst is filled into the tubes, which are placed in a shell that is filled with a coolant. In commercial applications, the internal tube diameter is typically in the range of 20 to 40 mm (see, e.g., US 4,921,681 A) or more than 40 mm (see, e.g., WO 2006/102189 A1).

To prepare ethylene oxide from ethylene and oxygen, it is possible to carry out the reaction under conventional reaction conditions as described, e.g., in DE 25 21 906 A, EP 0 014 457 A2, DE 23 00 512 A1, EP 0 172 565 A2, DE 24 54 972 A1, EP 0 357 293 A1, EP 0 266 015 A1, EP 0 085 237 A1, EP 0 082 609 A1 and EP 0 339 748 A2. Inert gases such as nitrogen or gases which are inert under the reaction conditions, e.g. steam, methane, and also optionally reaction moderators, for example halogenated hydrocarbons such as ethyl chloride, vinyl chloride or 1,2-dichloroethane can additionally be mixed into the reaction gas comprising ethylene and molecular oxygen.

The reaction gas preferably comprises a chlorine-comprising reaction moderator such as ethyl chloride, vinyl chloride or 1,2-dichloroethane in an amount of from 0 to 15 ppm by weight, preferably in an amount of from 0.1 to 8 ppm by weight, based on the total weight of the reaction gas. The remainder of the reaction gas generally comprises hydrocarbons such as methane and also inert gases such as nitrogen. In addition, other materials such as steam, carbon dioxide or noble gases can also be comprised in the reaction gas.

The concentration of carbon dioxide in the feed (i.e. the gas mixture fed to the reactor) typically depends on the catalyst selectivity and the efficiency of the carbon dioxide removal equipment. Carbon dioxide concentration in the feed is preferably at most 3 vol.-%, more preferably less than 2 vol.-%, most preferably less than 1 vol.-%, relative to the total volume of the feed. An example of carbon dioxide removal equipment is provided in US 6,452,027 B1.

The epoxidation of ethylene to ethylene oxide is usually carried out at elevated catalyst temperatures. Preference is given to catalyst temperatures in the range of 150 to 350 °C, more preferably 180 to 300 °C, particularly preferably 190 to 280 °C and especially preferably 200 to 280 °C.

The epoxidation is preferably carried out at pressures in the range of 5 to 30 bar. All pressures herein are absolute pressures, unless noted otherwise. The epoxidation is more preferably carried out at a pressure in the range of 5 to 25 bar, such as 10 bar to 24 bar and in particular 14 bar to 23 bar.

The epoxidation of ethylene is preferably carried out under conditions conducive to obtain a reaction mixture containing at least 2.3 vol.-% of ethylene oxide. In other words, the ethylene oxide outlet concentration (ethylene oxide concentration at the reactor outlet) is preferably at least 2.3 vol.-%. The ethylene oxide outlet concentration is more preferably in the range of 2.5 to 4.0 vol.-%, most preferably in the range of 2.7 to 3.5 vol.-%.

The epoxidation is preferably carried out in a continuous process. The epoxidation of ethylene can advantageously be carried out in a recycle process. After each pass, the newly formed ethylene oxide and the by-products formed in the reaction are removed from the product gas stream. The remaining gas stream is supplemented with the required amounts of ethylene, oxygen and reaction moderators and reintroduced into the reactor. The separation of the ethylene oxide from the product gas stream and its work-up can be carried out by customary methods of the prior art (cf. Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, vol. A-10, pp. 117-135, 123-125, VCH-Verlagsgesellschaft, Weinheim 1987).

The epoxidation of ethylene proceeds with less than 100% selectivity and is accompanied by the generation of carbon dioxide. It should be appreciated that emission of the carbon dioxide side product does not contribute to the carbon footprint of this process, as the starting ethylene is carbon neutral.

Hydrolysis Reaction of Ethylene Oxide

In an embodiment, step b) comprises a hydrolysis reaction of the ethylene oxide to produce ethylene glycol and/or ethylene glycol ethers. The ethylene glycol and the ethylene glycol ethers may be used in a large variety of industrial applications, for example in the fields of food, beverages, tobacco, cosmetics, thermoplastic polymers, curable resin systems, detergents and heat transfer systems.

The hydrolysis reaction of the ethylene oxide typically comprises reacting the ethylene oxide with water, suitably using an acidic or a basic catalyst. For example, for obtaining predominantly ethylene glycol (1,2-ethanediol) and less ethylene glycol ethers, the ethylene oxide may be reacted with a ten fold molar excess of water, in a liquid phase reaction in presence of an acid catalyst, e.g., 0.5 to 1.0 wt.-% sulfuric acid, based on the total reaction mixture, at 50 to 70 °C and at 1 bar absolute, or in a gas phase reaction at 130 to 240 °C and 20 to 40 bar absolute, preferably in the absence of a catalyst.

If the proportion of water is lowered, the proportion of ethylene glycol ethers in the reaction mixture is increased. The ethylene glycol ethers thus produced may be a d--ether, tri-ether, tetra-ether or a subsequent ether. Alternative ethylene glycol ethers may be prepared by converting the ethylene oxide with an alcohol, in particular a primary alcohol, such as methanol or ethanol, by replacing at least a portion of the water by the alcohol.

Amination Reaction of Ethylene Oxide

In an embodiment, step b) comprises an amination reaction of the ethylene oxide to produce ethanolamines and/or ethylene amines. Ethanolamine and may be used, e.g., in the treating (“sweetening”) of natural gas. Ethylene amines are used as solvents, stabilizers, starting materials for the synthesis of chelating agents, fungicides, micronutrients, synthetic resins, fibres, medicaments, inhibitors, and interface-active substances.

The amination of ethylene oxide in a first step provides ethanolamines, such as monoethanol amine and diethanol amine, which in a subsequent step may be aminated to give the desired ethylene amine. These reactions take place at a high pressure and a high temperature and lead to the formation of a number of side products as well.
To obtain ethanolamines, the amination reaction typically comprises reacting the ethylene oxide with ammonia, alkylamines such as monoalkylamines and dialkylamines, alkanolamines, or aromatic amines, preferably is ammonia. Anhydrous or aqueous ammonia may be used, although anhydrous ammonia is typically used to favor the production of monoethanolamine. For methods applicable in the conversion of the ethylene oxide into the ethanolamine, reference may be made to, for example US 4,845,296. The obtained ethanolamine preferably is monethanolamine or diethanolamine or a mixture of these two. Most preferably, the ethanolamine is monoethanolamine.

Amination of ethylene oxide with ammonia yields a stream comprising ammonia, monoethanolamine, diethanolamine and triethanolamine. Ethanolamines may be separated from this stream. Alternatively, the stream may be fed at least partially to a subsequent amination reaction with, e.g., ammonia, to obtain ethylene amines, such as ethylenediamine.

Suitable catalysts may contain a catalytically active compound on a solid support. Usually the catalyst contains as the catalytically active part at least one metal selected from the group consisting of nickel, chromium, cobalt, copper, ruthenium, iron, calcium, magnesium, strontium, lithium, sodium, potassium, barium, cesium, tungsten, silver, zinc, uranium, titanium, rhodium, palladium, platinum, iridium, osmium, gold, molybdenum, rhenium, cadmium, lead, rubidium, boron, and manganese, or mixtures thereof.

The temperature used during amination is generally between 120 and 300 °C, preferably in the range between 175 and 225 °C. The pressure used during amination is generally in the range of 8 to 40 MPa, preferably 15 to 30 MPa.

Hydrogenation of CO_x from Epoxidation of Ethylene

In an embodiment, the epoxidation reaction progresses under formation of CO_x as a side product, and the process further comprises subjecting said CO_x to hydrogenation to produce at least one of synthesis gas, methanol, formaldehyde and formic acid. While the carbon monoxide and/or carbon dioxide may be sequestered by, e.g., underground storage, it may be beneficial to subject said CO_x to hydrogenation to produce at least one of synthesis gas, methanol, formaldehyde and formic acid.

The synthesis gas, methanol, formaldehyde and/or formic acid thus produced may then be certified as carbon negative, and can at least partly displace their fossil-based counterparts and reduce the carbon footprint of chemical conversion processes making use of synthesis gas, methanol, formaldehyde and/or formic acid.

Claims

1. Process for the manufacture of styrene, said process comprising the steps of:
   a) subjecting a feedstock comprising a renewably-sourced ethanol to dehydration to produce a renewably-sourced ethylene stream; and
   b) reacting the renewably-sourced ethylene stream with benzene in an alkylation reaction to produce ethylbenzene, and subjecting the ethylbenzene to a dehydrogenation reaction to produce styrene.

2. Process according to claim 1, comprising blending the renewably-sourced ethylene with complementary ethylene prior to step b), the complementary ethylene not being obtained from renewably-sourced ethanol in accordance with step a).

3. Process for enhancing the environmental sustainability of styrene by blending or replacing a fossil-derived ethylene with a renewably-sourced ethylene to obtain a sustainability-enhanced ethylene and reacting the sustainability-enhanced ethylene with benzene in an alkylation reaction to produce ethylbenzene, and subjecting the ethylbenzene to a dehydrogenation reaction to produce styrene, wherein the renewably-sourced ethylene is obtained by subjecting a feedstock comprising a renewably-sourced ethanol to dehydration to produce the renewably-sourced ethylene stream.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/080094

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C2/68 C07C5/42 C07C11/04 C07C15/073 C07C15/46
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, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 8 735 515 B2 (COOPER SCOTT [US]; KHABASHESKU OLGA [US]; FINA TECHNOLOGY [US]) 27 May 2014 (2014-05-27) figure; column 6, lines 9-17 -----	1-3
X	US 2016/272665 A1 (DELGASS NICHOLAS WILLIAM [US] ET AL) 22 September 2016 (2016-09-22) paragraph [0013]; figure 2 -----	1-3
X	US 2022/204663 A1 (KASIREDDY MOHANREDDY [US] ET AL) 30 June 2022 (2022-06-30) paragraphs [0008], [0102], [0103] -----	1-3
X	US 2013/224808 A1 (BELL PETER SIMPSON [GB] ET AL) 29 August 2013 (2013-08-29) paragraphs [0023], [0063]; claims 19,20,31 -----	1-3

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

* Special categories of cited documents :

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search 26 January 2024	Date of mailing of the international search report 05/02/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Matés Valdivielso, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2023/080094

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 8735515	B2	27-05-2014	TW	201223968	A	16-06-2012
			US	2012046427	A1	23-02-2012
			WO	2012024112	A1	23-02-2012
US 2016272665	A1	22-09-2016	US	2016272665	A1	22-09-2016
			WO	2015061804	A1	30-04-2015
US 2022204663	A1	30-06-2022	US	2022204663	A1	30-06-2022
			WO	2020223335	A1	05-11-2020
US 2013224808	A1	29-08-2013	AU	2011328346	A1	30-05-2013
			CA	2815291	A1	18-05-2012
			CN	103180449	A	26-06-2013
			EP	2450450	A1	09-05-2012
			EP	2638169	A1	18-09-2013
			NZ	610399	A	29-05-2015
			RU	2013126201	A	20-12-2014
			US	2013224808	A1	29-08-2013
			WO	2012062633	A1	18-05-2012