PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 45/50

A1

(11) International Publication Number: WO 96/22266

(43) International Publication Date: 25 July 1996 (25.07.96)

(21) International Application Number: PCT/EP96/00268

(22) International Filing Date: 17 January 1996 (17.01.96)

(30) Priority Data:

375324	18 January 1995 (18.01.95)	US
375432	18 January 1995 (18.01.95)	US
375434	18 January 1995 (18.01.95)	US

(71) Applicants *(for all designated States except US)*: EXXON RESEARCH & ENGINEERING COMPANY [US/US]; 200 Park Avenue, P.O. Box 390, Florham Park, NJ 07932 (US). EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: HORVATH, Istvan, Tamas [HU/US]; 70 Valley View Road, High Bridge, NJ 08829 (US). KISS, Gabor [HU/US]; 4 Thomas Court, Hampton, NJ 08827 (US). MATTURRO, Michael, G. [US/US]; 41 York Street, Lambertville, NJ 08530 (US). DECKMAN, Harry, William [US/US]; 2 Woods Edge Court, Clinton, NJ 08809 (US). COOK, Raymond, A. [US/US]; 140 Blackbrook Road, Hampton, NJ 08827 (US). DEAN, Anthony, Marion [US/US]; 67 Cross Acres Drive, Hampton, NJ 08807 (US). HERSHKOWITZ, Frank [US/US]; 509 Lyons Road, Liberty Corner, NJ 07938 (US). VAN DRIESSCHE, Eddy [BE/US]; Krekelmuit 8, B-9900 Eeklo (BE).

(74) Agents: BAWDEN, Peter, Charles et al.; Exxon Chemical Limited, Exxon Chemical Technology Centre, P.O. Box 1, Abingdon, Oxfordshire OX13 6BB (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: HYDROFORMYLATION OF A MULTI-COMPONENT FEED STREAM

(57) Abstract

A process for the production of C_3 to C_6 aldehydes by hydroformylating a mixture of (i) C_2 to C_5 olefins and mixtures thereof, (ii) C_2 to C_5 alkynes and mixtures thereof and optionally (iii) cumulated dienes in the presence of a solution of a rhodium organophosphorus complex catalyst at a concentration of rhodium in solution of from 1 to 1000 ppm by weight, in particular the olefine is ethylene and the alkyne acetylene and the ratio of phosphorus to rhodium is greater than 30. The aldehydes are useful intermediates in the production of various alcohols, polyols and acids.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	**GB**	United Kingdom	**MW**	Malawi
AT	Austria	**GE**	Georgia	**MX**	Mexico
AU	Australia	**GN**	Guinea	**NE**	Niger
BB	Barbados	**GR**	Greece	**NL**	Netherlands
BE	Belgium	**HU**	Hungary	**NO**	Norway
BF	Burkina Faso	**IE**	Ireland	**NZ**	New Zealand
BG	Bulgaria	**IT**	Italy	**PL**	Poland
BJ	Benin	**JP**	Japan	**PT**	Portugal
BR	Brazil	**KE**	Kenya	**RO**	Romania
BY	Belarus	**KG**	Kyrgystan	**RU**	Russian Federation
CA	Canada	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SG**	Singapore
CH	Switzerland	**KZ**	Kazakhstan	**SI**	Slovenia
CI	Côte d'Ivoire	**LI**	Liechtenstein	**SK**	Slovakia
CM	Cameroon	**LK**	Sri Lanka	**SN**	Senegal
CN	China	**LR**	Liberia	**SZ**	Swaziland
CS	Czechoslovakia	**LT**	Lithuania	**TD**	Chad
CZ	Czech Republic	**LU**	Luxembourg	**TG**	Togo
DE	Germany	**LV**	Latvia	**TJ**	Tajikistan
DK	Denmark	**MC**	Monaco	**TT**	Trinidad and Tobago
EE	Estonia	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**UG**	Uganda
FI	Finland	**ML**	Mali	**US**	United States of America
FR	France	**MN**	Mongolia	**UZ**	Uzbekistan
GA	Gabon	**MR**	Mauritania	**VN**	Viet Nam

HYDROFORMYLATION OF A MULTI-COMPONENT FEED STREAM

FIELD OF THE INVENTION

This invention relates to hydroformylation methods for certain multicomponent syngas feed streams containing hydrogen, carbon monoxide, C_2 to C_5 olefins, and C_2 to C_5 alkynes.

BACKGROUND OF THE INVENTION

There is intensive research worldwide aimed at the utilization of natural gas as a petrochemical feed stock. The current use of natural gas is mainly restricted to the production of synthesis gas ("syngas", a mixture of carbon monoxide and hydrogen), and heat.

It has been long known, however, that methane can be converted to acetylene containing synthesis gas mixtures using short contact time acetylene burners. Co-producing ethylene or mixing ethylene with these acetylene rich feeds could provide a cheap, natural gas based feed stock. However, use of such co-produced feed streams has presented problems in certain processes.

Hydroformylation of highly purified olefins and syngas mixtures to aldehyde and alcohol products is well known (see B. Cornils "Hydroformylation Oxo Synthesis, Roelen Reaction" in "New Syntheses with Carbon Monoxide", Ed. J. Falbe, Springer Verlag, New York, 1980). When pure alcohol products are desired, the aldehyde products can be hydrogenated to the corresponding alcohol derivatives. A particularly useful catalyst has been described for the hydroformylation of pure light olefin feeds as a homogeneous oil soluble phosphine modified Rh catalyst (see, e.g., US Patents 3,527,809, 3,917,661, 4,148,830) which operates at lower pressures than other homogeneous catalysts, gives high normal to iso ratios in the hydroformylation of C_3 and higher olefins, and has been proven to be very effective with those pure olefin feeds. The use of such an oil soluble homogeneous Rh catalyst to hydroformylate purified ethylene feeds to propanal has been also described by Evans et al (J. Chem. Soc. (A) 1968, 3133), as well as Pruett et al (J. Org. Chem. 1968, 34, 327). There is a great need, however, for a stringent purification of the feed stock, because the activity of the catalyst is strongly inhibited by acetylene and other highly unsaturated hydrocarbons if they are present as impurities in commercial oxo feeds. These components must essentially be removed before hydroformylation (see B. Cornils "Hydroformylation

Oxo Synthesis, Roelen Reaction" in "New Syntheses with Carbon Monoxide", Ed J Falbe, Springer Verlag: New York, 1980, pp 64 and 73).

Highly purified feeds of syngas (mixtures of CO and H_2) and olefins are currently made in two separate processes. Light olefins are usually made by steam cracking and purified by cryogenic distillation and selective hydrogenation to remove even traces of acetylenes and dienes. The currently used highly purified olefin feeds contain less than 100 ppm and typically less than 10 ppm of these impurities. In fact, a large portion of the cost of ethylene currently produced for hydroformylation by steam cracking is associated with its purification. The syngas component can be made from a hydrocarbon, such as methane or a crude distillate, and oxygen in a partial oxidation (POX) reactor run in a mode that produces essentially no dienes or acetylenes. Even though the syngas made in the POX reactor contains only trace amounts of acetylenes and dienes it is also carefully further purified before being blended with the purified olefin feed.

Hydroformylation of pure acetylenes and of pure dienes with Co or Rh catalysts is also known (see US Patent 5,312,996, 1994; P W N M Van Leeuwen and C F Roobeek J Mol Catal 1985, US Patent 4,507,508, 1985; 31, 345, B Fell, H Bahrmann J Mol Catal 1977, 2, 211, B Fell, M Beutler Erdöl und Kohle - Erdgas - Petrochem 1976, 29 (4), 149, US Patent 3,947,503, 1976, B Fell, W Boll Chem Zeit 1975, 99(11),452; M Orchin, W Rupilius Catal Rev 1972, 6(1), 85; B Fell, M Beutler Tetrahedron Letters 1972, No 33, 3455, C K Brown and G Wilkinson J Chem Soc (A) 1970, 2753, B Fell, W Rupilius Tetrahedron Letters 1969, No 32, 2721, F H Jardine et al Chem and Ind 1965, 560, H Greenfield et al J Org Chem 1957, 22, 542, H Adkins and J L R Williams J Org Chem 1952, 71, 980) The hydroformylation of these highly unsaturated compounds with cobalt catalysts is slow even at high temperatures and pressures (145 - 175 °C, 20 - 30 MPa) Furthermore, the reaction often yields side products and results in runaway reactions with sudden temperature and pressure surges The hydroformylation of olefins is severely inhibited by acetylenes since these compounds form very stable adducts with cobalt carbonyl Stoichiometric amounts of acetylenes can effectively transform the cobalt catalyst into these catalytically inactive acetylenic adducts (H Greenfield et al J Org Chem 1957, 22, 542) With conventional Rh catalysts the reported reaction conditions and reaction rates are far from being practical for any commercial use Fell typically used 17 - 23 MPa pressures using PPh3/Rh catalyst, yet high conversions required 2 to 5 hour reaction times Wilkinson achieved high conversion in the hydroformylation of hexyne-1 at 4 8 MPa pressure but only with a reaction time of 12 hours Van Leeuwen and Roobeek applied conditions of 1 2 MPa, 95 - 120 °C, and P/Rh ratios of 10 or below in the hydroformylation of butadiene but

observed low activities (orders of magnitude below that for olefins). In US Patent 3,947,503 a two stage process is described to hydroformylate 1,3-butadiene. In the first stage PPh_3/Rh catalyst is used in the presence of alcohols or diols to make the acetals of the unsaturated C_5-aldehyde. In the second stage this intermediate is hydroformylated using Co catalysts. The process disclosed in US Patent 4,507,508 also claims the conversion of conjugated dienes with organic acid or ester promoted P/Rh catalyst in the presence of alcohols. US Patent 5,312,996 describes a polyphosphite ligand modified Rh catalyst for the conversion of 1,3-butadiene. When using a two stage process for the hydroformylation of 1,3-butadiene with the disclosed catalyst more severe conditions are recommended in the second stage to ensure acceptable conversions. This later patent also describes 1,3-butadiene as a strong inhibitor in the conversion of alpha-olefins. In the co-conversion of alpha-olefins with 1,3-butadiene oxo aldehyde products of both the alpha-olefins and 1,3-butadiene were produced.

As mentioned, acetylenes and dienes act as strong inhibitors/poisons of catalysts in the hydroformylation of alpha-olefins and their removal is required from oxo feeds European Patent Application No. 0225143 A2 discloses a method for the production and utilization of acetylene and ethylene containing syngas mixtures. One of the disclosed utilization schemes is to produce propanal by hydroformylation, but acetylene first must be removed from the feed by selective hydrogenation to ethylene over a heterogeneous metal oxide or sulfide catalyst. US Patent 4,287,370 also teaches that inhibitors such as 1,3-butadiene must be removed from C_4-olefin feed stocks by selective hydrogenation prior to hydroformylation using $HRh(CO)(PPh_3)_3$ as a catalyst. German patent, DE 2638798, teaches that the removal of acetylenes and dienes is necessary in order to ensure acceptable catalyst life in the hydroformylation of olefins with a phosphine modified rhodium catalyst. In one of the most often cited sources (B. Cornils "Hydroformylation - Oxo Synthesis. Roelen Reaction" in "New Syntheses with Carbon Monoxide", Ed. J. Falbe, Springer Verlag, New York, 1980, p. 73) acetylenes and dienes are referred to as "classical catalyst poisons" for the phosphine modified Rh oxo catalysts. Acetylenes and dienes are also reported to be strong poisons in the hydroformylation of olefins with cobalt catalysts (V. Macho and M. Polievka Rau. Roc. 1976, 18(1), 18; US Patent 2,752,395).

Known catalytic processes converting acetylene and ethylene containing syngas mixtures either produce products other than propanal or the conditions used and /or the reaction rates achieved are far from being practical. Thus, for example, European Patent Application No. 0,233,759 (1987) teaches the conversion of acetylene and ethylene containing syngas (a mixture of acetylene, ethylene, CO, and H_2 with a ratio of 6:3:30:61, respectively) into a mixture of acrylate and propionate esters in the presence of an alcohol

using a Rh catalyst. When using a PPh3 modified Rh oxo catalyst to convert the same feed at a P/Rh ratio of 10.6 under otherwise identical conditions, the essentially dead catalyst (turnover frequency of $1.5x10^{-4}$ mol product/mol Rh/sec, and total turnover of 13 in 24 hours) described in European Patent Application No. 0,233,759 (1987) produces some propanal and acetone in a molar ratio of 90 to 1 with traces of methyl ethyl ketone and methyl propionate. It has been reported by T. Mise et al. (Chem. Lett. 1982, (3), 401) that syngas mixtures containing acetylene and ethylene yield α,β-unsaturated ethyl ketones in the presence of a Rh catalyst, however, no phosphine is present in the catalyst. Observed catalyst activities are very low, on the order of 5 turnover/h, or $1.39x10^{-3}$ mol product/mol Rh/sec even though the concentration of ethylene in the gas feed is high, 41.7 v.%. The total turnover reported by Mise is only 30 in 6 hours.

Thus it would be desirable if methods could be found to enable the processing of oxo/hydroformylation feed streams using rhodium based catalysts that contain olefins and alkynes, particularly ethylene and acetylene. The present invention addresses these needs.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 describes a hydrotreating guard bed to reduce the level of multiunsaturates in a multicomponent syngas using a rhodium complex as a reagent in a scrubber guard bed.

Figure 2 describes a two-stage oxo process for the hydroformylation of multi-component syngas mixtures.

Figure 3 describes an integrated process for aldehyde product separation and alkyne-olefin recovery with alkyne-olefin recycle.

SUMMARY OF THE INVENTION

The present invention provides for methods of using a multicomponent syngas containing mixed unsaturated hydrocarbon feeds having both an olefin (particularly ethylene) and more highly unsaturated hydrocarbons, particularly alkynes (particularly acetylene), cumulated dienes (particularly allene) and mixtures thereof, rather than single type feed streams, in hydroformylation reactions carried out in the presence of certain rhodium complexes as catalysts. As a benefit, the invention allows for the co-conversion of acetylene and ethylene using rhodium based catalyst technologies and provides new feed stock and processing options, and simplified production schemes for the synthesis of the corresponding product aldehydes, particularly propanal.

Thus, the present invention provides a process for the production of C_3 to C_6 aldehydes, comprising hydroformylating a mixture containing

- - (a) C_2 to C_5 olefins and mixtures thereof, and
- - (b) (i) C_2 to C_5 alkynes and mixtures thereof or (ii) C_3 to C_5 cumulated dienes and mixtures thereof or (iii) mixtures of (i) and (ii),

with CO, H_2 and a solution of a rhodium complex catalyst produced by complexing Rh and an organophosphorus compound at a concentration of Rh in solution from 1 to 1000 ppm by weight.

The present invention also provides a process for the production of C_3 to C_6 aldehydes, comprising hydroformylating a mixture containing

- - (a) C_2 to C_5 olefins and mixtures thereof, and
- - (b) (i) C_2 to C_5 alkynes and mixtures thereof or (ii) C_3 to C_5 cumulated dienes and mixtures thereof or (iii) mixtures of (i) and (ii),

with CO, H_2 and a solution of a rhodium complex catalyst produced by complexing Rh and an organophosphorus compound wherein the catalyst solution has a P/Rh atom ratio of at least 30.

The present invention also provides a process for the production of C_3 to C_6 aldehydes, comprising hydroformylating a mixture containing

- - (a) C_2 to C_5 olefins and mixtures thereof, and
- - (b) (i) C_2 to C_5 alkynes and mixtures thereof or (ii) C_3 to C_5 cumulated dienes and mixtures thereof or (iii) mixtures of (i) and (ii),

with CO, H_2 and a solution of a rhodium complex catalyst produced by complexing Rh and an organophosphorus compound wherein the catalyst solution has a P/Rh atom ratio greater than the value R_L wherein

$$R_L = R_B + \frac{(30 - R_B) \bullet 10^{(pKa_{TPP} - pKa_L)}}{e^{(\Delta S_B / R)}}$$

wherein R_B is the P/Rh ratio sufficient for a catalytically active Rh complex, pKa_{TPP} is the pKa value for triphenylphosphine, pKa_L is the pKa value for the triorganophosphorus compound, R is the gas constant, and ΔS_B is 35(N-1) cal/mole/°K, wherein N is the number of P–Rh attachments per ligand molecule.

Hydroformylation, as described above, produces the corresponding C_3 to C_6 aldehydes.

Typically, the P/Rh atom ratio R_B for the catalytically active Rh complex is between 1 and 3. Typically, the rhodium complex catalyst is an oil soluble rhodium complex catalyst produced by complexing in solution a low valence Rh and an oil soluble triorganophosphorus compound. Typically, the catalyst solution may be prepared with an oily solvent such as aliphatic or aromatic hydrocarbons, esters, ethers, aldehydes, the condensation side products of the product oxo aldehydes, etc.

The present invention also provides for the production of the corresponding derivatives of the aldehydes produced as provided above, including alcohols, acids, aldol dimers, and various hydrogenation and oxidation products produced from the aldol dimers.

We have also found that the presence of acetylene stabilizes the hydroformylation catalyst.

The present invention may suitably comprise, consist or consist essentially of the elements disclosed herein and may be practiced in the absence of any step not specifically disclosed as required.

DETAILED DESCRIPTION OF THE INVENTION

The headings herein are solely for convenience and are not intended to limit the invention in any way. In addition, solely for convenience the numbering in Figures and throughout the text is as follows: process (e.g., reactant and product) streams are numbered in hundreds, and means for carrying out a process or operation (e.g., units or devices) are numbered in tens. The first digit of each identifies the figure to which it corresponds.

The present invention pertains to processes that use multicomponent synthesis gas. A multicomponent synthesis gas (MCS) mixture is defined as gas mixtures containing carbon monoxide, hydrogen, olefins (with a general formula of C_nH_{2n} and with a functional group of C=C) having from 2 to 5 carbon atoms, and a more highly unsaturated hydrocarbon such as alkynes (with a general formula of C_nH_{2n-2} and with a functional group of C≡C) having from 2 to 5 carbon atoms or cumulated dienes (with a general formula of C_nH_{2n-2} and with a functional group of C=C=C). MCS mixtures can optionally contain other unsaturated hydrocarbons such as and conjugated dienes (with a general formula of C_nH_{2n-2} and with a functional group of C=C-C=C) having 3 to 5 carbon atoms, enynes (with a general formula of C_nH_{2n-4} and with a functional group of C=C-C≡C) and diynes (with a general formula of C_nH_{2n-6} and a functional group of C≡C-C≡C) having 4 to 5 carbon atoms. MCS mixtures

may also contain inert components, e.g., nitrogen, carbon dioxide, functionally inert hydrocarbons such as alkanes and aromatic hydrocarbons, and water vapor. As used herein the term "olefin" includes alkenes and excludes dienes; dienes, when present, are referred to separately.

In the following discussions "monounsaturates" are understood as a subgroup of hydrocarbon MCS components which have one unsaturated functionality that is olefins or alkynes. The "C_2 unsaturates" are ethylene or acetylene individually or combined. The "multiunsaturates" are a subgroup of hydrocarbon MCS components which have at least two multiple carbon-carbon bonds i.e. dienes, diynes, and enynes as defined herein, taken individually or in any combination.

The present invention provides methods for converting certain MCS feeds by reassembling its main components, hydrogen and carbon monoxide (i.e., syngas), C_2-C_5 alkynes, particularly acetylene, and C_2-C_5 olefins, particularly ethylene, by hydroformylation (oxo reaction).

One embodiment of the process of the present invention provides a method for using a multicomponent syngas feed containing at least carbon monoxide, hydrogen, and monounsaturated hydrocarbon reactants of olefinic hydrocarbons having from 2 to 5 carbon atoms (i.e. ethylene, propylene, butenes, and pentenes), and alkynes having from 2 to 5 carbon atoms (such as, e.g., acetylene and methyl acetylene), in a rhodium catalyzed low pressure oxo conversion process. These monounsaturated alkynes and olefins include the individual C_2-C_5 alkyne components and olefin components, as well as mixtures of the C_2-C_5 alkyne components and mixtures of the C_2-C_5 olefin components. In a preferred embodiment, the major monounsaturated hydrocarbon reactants are essentially ethylene and acetylene. These reactants are fed into the process as components of a multicomponent syngas which may also contain, depending on its preparation method, reactive C_3 to C_5 monounsaturates and C_3 to C_5 multiunsaturates as minor components, and functionally inert materials in varying quantities such as carbon dioxide, water vapor, nitrogen, and functionally inert hydrocarbons (such as alkanes and aromatics).

Multicomponent syngas containing substantial amounts of inert (and functionally inert) components may be referred to as dilute multicomponent syngas. Dilute multicomponent syngas can embody any multicomponent syngas feed wherein the reactive components (CO, H_2, olefin, alkyne) may be present together with substantial amounts of inert components. The use of feed streams having substantial diluent levels is desirable in that these feed streams

may be available at substantial discount relative to the cost of highly purified components. For example, the olefin contained in cat cracker light ends or in steam cracker furnace effluent can be available at substantial discount relative to purified olefins. Likewise, acetylene and syngas are less costly if they can be obtained without complete purification. Furthermore, partial oxidation (POX) processes can be less costly if air is used as feed instead of oxygen. Syngas or multicomponent syngas from such an air-blown POX might be characterized as dilute multicomponent syngas due to the substantial levels of included N_2. In principal, the amount of inert components present in a dilute multicomponent syngas may be any value, even reaching 99% of the feed stream. Typically, inert component levels in a dilute multicomponent syngas are between 1% and 80% of the stream. Table 2 (Example 1) shows an example of hydroformylation of a dilute multicomponent syngas having 63% of inert components, including N_2, CO_2, CH_4, and C_2H_6.

Certain trace components in the multicomponent syngas feed of the overall process referred to herein as "multicomponent process feed" are known to be detrimental in the oxo reaction. Some are irreversible catalyst poisons , e.g., sulfur compounds such as H_2S and COS. Others cause reversible poisoning or accelerated catalyst deactivation. This later group includes components like halides, cyanides, oxygen, and iron carbonyls. The concentration of these detrimental components can be adjusted by a variety of techniques known in the art to provide an acceptable multicomponent syngas feed to the oxo reactor or unit referred to herein as "multicomponent oxo reactor feed".

Multicomponent syngas mixtures are available from a variety of different sources. A benefit of the present invention is that any mixed acetylene-ethylene syngas mixture can be used as a feed stock in the processes of the present invention.

A variety of methods exist to manufacture multicomponent synthesis gas mixtures useful in the process of the present invention. One is to blend a stream containing syngas (a mixture of CO and H_2) with a stream containing a mixture of acetylene, ethylene, and optionally other unsaturated hydrocarbons. Both of these streams can be obtained from conventional petrochemical processes. The syngas (CO and H_2) containing stream can be produced by conventional partial oxidation (POX). Light monounsaturates (C_2-C_5) containing ethylene and acetylene as major unsaturated hydrocarbon components can be obtained from petrochemical processes such as steam cracking or acetylene manufacture, or by modification of one of the known processes used to manufacture acetylene or syngas. Thus acetylene can be formed using a partial oxidation process that applies a burner to react methane-oxygen mixtures. Acetylene burners fed with about two to one molar ratio of

methane and oxygen can directly produce an acetylene rich gas mixture that contains ethylene as well as CO and hydrogen. Quenching the reaction with naphtha can further increase the concentration of acetylene and ethylene in the acetylene burner product stream. Ethylene or syngas can also be added to acetylene rich mixtures to adjust the molar ratios of the components. An advantage of the foregoing is that it allows for the utilization of an abundant feed stock, such as natural gas, and eliminates the need of elaborate and expensive separation and purification of oxo feeds often resulting in significant yield losses and added expense.

In order to maintain the partial pressure of acetylene below the safety limit, a part of the acetylene may be scrubbed from MCS feeds before compressing them to the reaction pressure for the oxo reactor. Alternatively, acetylene-containing streams can be diluted with other feed components, e.g., ethylene, carbon monoxide, hydrogen or mixtures thereof.

Multicomponent syngas streams entering the oxo hydroformylation reactor or reaction zone (multicomponent oxo reactor feeds) in the process of the present invention contain C_2 to C_5 monounsaturates, among which the ethylene to acetylene ratio is in a range from 1:100 to 100:1, preferably 1:10 to 10:1. Typically, the mixture contains an amount of olefins that is at least 40% of the total unsaturates. The amount of CO and H_2 in the multicomponent oxo reactor feed, with respect to the amount of monounsaturates is preferred to be at levels of at least about that required for the stoichiometric conversion of monounsaturated hydrocarbons in the oxo reaction. A stoichiometric conversion of these species requires that the mole percent of CO be equal to the sum of the mole percents of monounsaturates. Similarly, for stoichiometric conversion, the mole percent of H_2 should be equal to the sum of the mole percents of C_2 to C_5 olefins plus twice the mole percents of C_2 to C_5 alkynes. It is preferred that the CO and H_2 be present in the multicomponent oxo reactor feed in a range from half to 100 times that required for stoichiometric conversion. It is more preferred that the concentrations of CO and H_2 be in the range from 1 to 10 times that required for a stoichiometric conversion.

Subject to these requirements, H_2/CO ratios in the multicomponent synthesis gas entering the oxo reactor (i.e. in the multicomponent oxo reactor feed) can range from 1:1 to 100:1, preferably 1:1 to 50:1, more preferably 1:1 to 10:1. While the presence of excess volumes of H_2 is preferred from a chemistry perspective, a large excess of H_2 of greater than 10 is not desirable from a materials handling perspective and can result in unnecessary expense in unit operation.

A range of composition values, as well as a typical composition for the principle species present in multicomponent syngas mixtures entering the oxo reactor (i.e. in the multicomponent oxo reactor feeds) for the process of the present invention are given in Table 1.

Table 1. Multicomponent oxo reactor feed compositions for the principal components

Principal Components	Composition Range (v. %)	Typical Composition (v. %)
CO	1 - 50	25
H_2	1 - 98	50
Ethylene	0.1 - 35	15
Acetylene	0.1 - 35	10

Multicomponent syngas mixtures produced by, e.g., steam cracking or by partial oxidation can contain a variety of molecular species which are detrimental to the hydroformylation process or are known to deactivate oxo catalysts. For example, rhodium metal complex hydroformylation catalysts are known to be poisoned by certain sulfur containing molecules (e.g., H_2S, and COS) which irreversibly bind to the metal center. Such poisons can be removed by use of common chemical and chemical engineering techniques such as the use of guard beds, particularly guard beds containing zinc oxide.

The streams used with the present invention may also contain multiunsaturates having 3 to 5 carbon atoms. Their concentrations are typically less than 5 mole% of the total unsaturated hydrocarbon fed to the hydroformylation. Catalysts discussed herein as being active for the hydroformylation of olefins and alkynes will similarly be active for the hydroformylation of olefins and multiunsaturates. Highly unsaturated components such as these multiunsaturates can be inhibitors in the oxo conversion of olefins. They may reduce the activity of the oxo catalyst by associating very strongly with the metal and thus diminishing the activity of the catalyst toward the hydroformylation of olefins. Therefore, the quantities of multiunsaturates are preferably less than 5% of the total unsaturated hydrocarbon fed to the hydroformylation. More preferably, multiunsaturates should be present in hydroformylation feed in amounts less than 1 mole% of total unsaturates. Examples 4 and 8 demonstrate the hydroformylation of multicomponent syngas mixtures that contain olefins and multiunsaturates (specifically, allene). An exception to the foregoing preferences on multiunsaturate

concentrations is the group of non-conjugated, non-cumulated dienes (diolefins), for which there are no restrictions.

Generally speaking, the multicomponent oxo reactor feed streams preferably contain monounsaturates. Multiunsaturated hydrocarbons containing conjugated and cumulated diene and enyne type unsaturation are considered less desirable. These multiunsaturates may be removed from multicomponent process feeds or their concentrations may be reduced before contact with the hydroformylation catalyst. Although multicomponent syngas products generally do not require treatment before their use in the processes of the present invention, feed streams containing multiunsaturates in higher concentration than the above preferred concentrations may be treated, segregated or diluted with streams comprising substantially CO, H_2, monounsaturates, and inerts.

MULTIUNSATURATES REMOVAL

Multicomponent process feeds can be treated if necessary before entering the oxo reactor (i.e. prior to hydroformylation) if the concentration of the above specified multiunsaturated inhibiting components is too high. Mild selective hydrogenation, for example, using heterogeneous catalysts (e.g., Pd on alumina, or mixed oxide and sulfide catalysts as described in EP Application 0,225,143) can convert these reactive hydrocarbons to olefins and alkanes. These conventional heterogeneous hydrotreating methods, however, have drawbacks. For example, in heterogeneous systems high concentrations of unsaturated hydrocarbons (i.e. olefins, alkynes, and multiunsaturates) with high concentrations of hydrogen present a hazard of a highly exothermic runaway reaction. Catalyst selectivity, and other plant operation issues provide further incentives to seek alternative solutions.

Therefore, another embodiment of the present invention provides a selective, liquid phase process to address the problems associated with the application of the known heterogeneous catalysts. The liquid phase used in the process can be a homogeneous phase or a pumpable, solids-containing slurry. Applicants have found that the Rh catalyst used in the hydroformylation process of the present invention is suitable for the selective conversion of the foregoing multiunsaturated hydrocarbon components to olefins when the complex is used not as a catalyst but as a stoichiometric reagent in a separate pre-treatment step. The preferred reagent is the organophosphorus modified rhodium catalyst of the oxo/hydroformylation reactor described more detail in "Rh OXO CATALYST" below. In a preferred embodiment a two step process is used to convert excess multiunsaturates in the MCS to olefins and alkanes. In the first step of the process the Multicomponent Syngas is

contacted with a solution containing the liganded rhodium complex as a reagent. The strong preferential binding of multiunsaturates to the rhodium complex serves to extract them from the MCS and into the solution where they are held as bound species on the rhodium. This gas/liquid "scrubbing" effectively removes the multiunsaturates from the MCS feed. The Rh complex essentially functions as a stoichiometric reagent, binding the multiunsaturated hydrocarbons from MCS during the contacting. In a separate, second step the multi-unsaturates are converted to the corresponding olefins and the rhodium complex is regenerated by contacting the complexed multiunsaturates containing solution with a gas of high hydrogen and low carbon monoxide content for an amount of time sufficient to effect the conversion of multiunsaturates.

If such multiunsaturates hydrogenation was carried out under conventional hydroformylation conditions, i.e. at CO partial pressures of 10-1000 kPa, the conversion of these strongly bound species to olefins would be slow (see Example 4), such that the required rhodium concentrations would be uneconomical. However, we have discovered that the conversion of these multiunsaturates can be substantially accelerated under conditions of higher hydrogen, and especially, lower CO partial pressures than conventional rhodium hydroformylation. The complexed multiunsaturates-containing Rh solution can be regenerated in a separate reactor, with a hydrogen rich gas, i.e., a gas having high hydrogen and low CO concentrations or pure hydrogen. During this regeneration, the Rh complex is returned to its multiunsaturate-free form, while the multiunsaturates are hydrogenated to the corresponding olefins and alkanes. Thus allene, for example, is hydrogenated during this process first to propylene, while butadienes are hydrogenated to butenes. In this regeneration hydrotreating step some of the olefins formed from multiunsaturates will be further hydrogenated to the corresponding alkanes. The hydrogenation rate in the regeneration step can be adjusted by adjusting the partial pressures of hydrogen and CO. Higher partial pressures of hydrogen will increase the rate of hydrogenation. On the contrary, increasing partial pressures of CO will reduce the hydrogenation activity of the catalyst. The rate and selectivity can be conveniently controlled by adjusting the partial pressure of CO in the hydrotreating reactor.

The benefit of the herein described process is that the composition of the scrubbing solution used for the stoichiometric removal of multiunsaturates can essentially be the same as used for the catalytic oxo step. Any level of multiunsaturates removal can be accomplished. The multiunsaturated hydrocarbons (e.g. allene or vinyl acetylene) are preferentially removed from the gas phase because they bind stronger than the monounsaturates, particularly olefins. Since the stronger binding components are the stronger inhibitors in the oxo conversion of

monounsaturates, in particular in the oxo conversion of olefins, the process removes the strongest inhibitors first and produces a purified, multiunsaturate-deficient MCS, which is preferred as oxo/hydroformylation reactor feed. An additional advantage of using the rhodium oxo catalyst solution for the pre-treatment of MCS hydroformylation feed is that it is unnecessary to rigorously control losses of rhodium complex due to entrainment in the MCS gas phase, because the downstream hydroformylation reactor system must have means to effectively capture this Rh complex. Furthermore any Rh compound carried over by the MCS stream will not contaminate the catalyst in the oxo reactor since the compositions are essentially the same.

By way of example, Figure 1 shows Absorber 11, in which the multiunsaturates-containing MCS feed (101) is contacted with a multiunsaturates-depleted solution of the oil soluble rhodium complex (105). This absorber is analogous to guard beds of sacrificial catalyst that are sometimes used in heterogeneous catalysis. The multiunsaturates-depleted MCS stream (102) emerges from the absorber to be sent to hydroformylation (shown here as two reactors (13 and 14) in series, each with pumparound cooling (107 and 109) and reactor effluents (108 and 110)). Unlike the "guard bed" of heterogeneous catalysis, the multiunsaturates-containing "sacrificial" catalyst of this process is a pumpable liquid phase solution of a Rh complex (106) that is recovered at the bottom of the absorber. The complexed multiunsaturates-containing solution (106) is pumped into a regeneration reactor (12) in which it is treated with a hydrogen-containing gas (104). In the regeneration reactor, the multiunsaturates-free rhodium complex is recovered by the hydrogenation of the complexed multiunsaturates to olefins and alkanes. A gaseous purge stream (103) from the regeneration reactor is used to preserve high concentrations of hydrogen. The regenerated, multiunsaturates-depleted solution of the Rh complex (105) is returned from the regenerator (12) to the absorber (11). To the extent that the olefin and alkane products of multiunsaturates hydrogenation remain dissolved in the catalyst solution, they will be transferred back to the MCS stream during contact with the catalyst solution in absorber (11).

The temperature in the absorber (11) is maintained in the range of 0 to 150 °C, preferably between 20 to 60 °C. If the temperature exceeds these limits, the Rh complex can decompose unacceptably fast. Also, at higher temperatures there is the possibility of high reactivity and exotherms if the absorber has locations where both the Rh containing solution and MCS are depleted in inhibitors. This would be true, for example, at the top of a counter-current absorber. Lower temperatures are acceptable. However, the rate of equilibration between the Rh complex and inhibitors will become limiting at some low temperatures. Furthermore, low temperatures can entail an extra cost of refrigeration with no added

advantage from a process point of view. The pressure in absorber 11 is kept preferably at less than about 5 MPa with a partial pressure of acetylene below the safety limit of 0.2 MPa. In a preferred embodiment the absorber is positioned immediately before the oxo/hydroformylation reactor.

The temperature in the regenerator (12) is maintained in the range of 50 to 150 °C, more preferably between 80 to 125 °C. The pressure in the regenerator is typically limited by engineering, and economic factors. Higher hydrogen pressures accelerate the regeneration of the multiunsaturates-free Rh complex and the hydrogenation of the scrubbed and complexed multiunsaturates, permitting smaller regeneration vessels and smaller quantities of rhodium complex. Preferably the pressure in the regenerator is maintained in the range of about 0.1 to 50 MPa, and more preferably in the range of about 1 to 10 MPa. The liquid feed to the regenerator leaves the absorber (11) without any treatment. The gas feed is a hydrogen containing gas, which can be either essentially pure hydrogen or a gas mixture enriched in hydrogen and deficient in CO. Other guard beds designed to remove irreversible poisons of the Rh oxo catalyst such as sulfur compounds, halides, cyanides, iron carbonyls and the like, should also be used to pretreat the MCS feed stream to the multi-unsaturates absorber (11). The hydrogen-rich feed gas to the regenerator (12) should also be essentially free of the foregoing irreversible poisons, and other detrimental compounds to the Rh complex. The addition of pure, sulfur free hydrogen is preferred in the gas feed to the regenerator. The rate and selectivity of the hydrogenation step toward producing olefins from multiunsaturates and alkynes can be controlled by adjusting the partial pressure of CO. The H_2/CO partial-pressure ratio in the regenerator should be 10 or higher, preferably 50 or higher. Higher CO partial pressures lead to higher selectivity to olefins but reduced rate to multi-unsaturates conversion. In certain cases the CO dissolved in the complexed multi-unsaturates-containing solution (106) can provide a sufficient partial pressure of CO in the regenerator (12). If necessary, CO can be co-fed with hydrogen containing gas into the regenerator or gas mixtures deficient in CO and enriched in hydrogen can be used.

The absence of CO does not have a destabilizing effect on the Rh complex but does affect the rate and selectivity of the hydrogenation of the unsaturated hydrocarbons present in the regenerator. With no CO present all unsaturated hydrocarbons, including olefins, tend to be hydrogenated to alkanes. It is therefore desirable to maintain CO concentration in the regenerator at a level sufficient to preferentially hydrogenate the multiunsaturates only to olefins in order to achieve an economic compromise between faster regeneration of the multiunsaturates-free Rh complex (therefore smaller equipment size, and smaller Rh load) and loss of C_2 to C_5 olefin source due to reduced selectivity. The separation of the

multiunsaturates from the main stream of the multicomponent syngas improves the overall selectivity of the process since the multiunsaturates are treated separately so that the bulk of ethylene and acetylene in MCS is not exposed to the hydrogenation conditions appropriate for rapid conversion of multiunsaturates.

The flow rate of catalyst solution to the absorber is set to meet the concentration limits given for multiunsaturate of the multicomponent oxo reactor feed, as described previously. The flow rate of rhodium should be set at a sufficient level to stoichiometrically combine with the amount of multiunsaturates to be removed. Thus, a treat ratio can be defined as the ratio of the flow rate of rhodium to the absorber (expressed as moles per unit time) to the flow rate of multiunsaturates to be removed (also as moles per unit time). For an ideal absorption system, this treat ratio can be exactly 1.0 for perfect removal of only. the desired multiunsaturates. Treat ratios should be between 0.5 and 50 in the current invention, preferably between 1 and 10. Higher treat ratios would be recommended if a significant fraction of the rhodium complex is inactive, or if it is desired to remove and convert some fraction of the alkyne component of the MCS in addition to the multiunsaturates.

Conditions (temperature, pressure, residence time, etc.) in the regenerator are set such that conversion rate of multiunsaturates equals the rate at which they are being carried into the regenerator by catalyst solution (which, in turn, equals the rate of multi-unsaturates removal in the absorber). Example 4 includes selected rates of multiunsaturates conversion that can be used by one skilled in the art of chemical engineering to specify operating conditions of the regenerator. The scrubbing solution may be essentially the same as that of the catalyst solution used in the oxo reactor step or any soluble or slurry phase catalyst that achieves the same effect under the conditions herein. Preferably the absorption process uses the spent catalyst solution from the oxo reactor as a scrubbing solution before its final disposal, and/or recycling.

An advantage of the use of the above described treatment from the aspect of the process of the present invention is that the multiunsaturates are not converted in the oxo reactor therefore do not tie up a large amount of active catalyst. They are removed from the main feed stream and separately converted into olefins. The formed olefins are then preferably recycled to the multicomponent oxo reactor feed, and hydroformylated in the oxo reactor. A further advantage of the use of the present absorption-regeneration process for multiunsaturates conversion is in the elimination of the hazard of runaway hydrogenation reactions associated with hydrogenation of highly unsaturated hydrocarbons. This hazard is eliminated in the practice of the current invention because the amount of unsaturated species

in the reactor is limited to the amount carried in bound to the rhodium or physically dissolved in the solvent. Thus, each Rh site is limited to a very limited turnover before it runs out of unsaturated species to hydrogenate. Under this situation, even a rapid increase in reaction rate can only result in the conversion of a limited amount of unsaturated species and so the resulting heat release is strictly limited.

Rh OXO CATALYST

In the process of the present invention the oxo/hydroformylation catalyst is a rhodium complex catalyst, preferably an oil soluble rhodium complex catalyst. The oil soluble catalyst is typically formed by a complexation reaction in solution between a low valence rhodium, an oil soluble organophosphorus compound, preferably a triorganophosphorus compound or a mixture of such compounds, and carbon monoxide. Under reaction conditions the Rh central atom may be complexed with other species present in the reaction mixture, such as ethylene, and other olefins (e.g., propylene), acetylene, and other alkynes (e.g. methyl acetylene), dienes, and other highly unsaturated hydrocarbons (e.g., allene, butadienes, vinyl acetylene, etc.), and hydrogen, which also can act as ligands.

The preferred triorganophosphorus compounds suitable for the preparation of the Rh complex catalyst for the use in the oxo reactor in the present invention belong to the group of oil soluble triarylphosphines, trialkylphosphines, alkyl-diarylphosphines, aryl-dialkylphosphines, trialkylphosphites, triarylphosphites, containing at least one phosphorus atom per molecule. These should be capable of complexation with Rh by the virtue of having a lone pair of electrons on the phosphorus. Non-limiting examples of such oil soluble triorganophosphorus compounds for use in the catalyst include triarylphosphines, such as triphenylphosphine or tri-p-tolylphosphine, trialkylphosphines, such as trioctylphosphine or tricyclohexylphosphine, or alkyl-diarylphosphines, such as octyldiphenylphosphine or cyclohexyldiphenylphosphine, or aryldialkylphosphines, such as phenyldioctylphosphine or phenyldicyclohexylphosphine, etc. The triorganophosphorus compounds that can serve as ligands can also be other phosphorus containing compounds such as triorganophosphates, e.g., trialkylphosphites such as trioctylphosphite, triarylphosphites such as tri-p-tolylphosphite. In addition to monodentate phosphorus ligands, bidentate compounds such as diphos (bis(diphenylphosphino)ethane) can be used. An extended list of suitable phosphine ligands is given in Falbe's book at p. 55 - 57. Preferably, the oil soluble triorganophosphorus compound is a trialkylphosphine such as tricyclohexylphosphine and trioctylphosphine or a triarylphosphine such as triphenylphosphine. However other ligands such as

phenyldicyclohexylphosphine, diphenylcyclohexylphosphine, phenyldioctylphosphine, tri-p-tolylphosphine, trinaphthylphosphine, phenyl-dinaphthylphosphine, diphenyl-naphthylphosphine, tri-(p-methoxyphenyl)phosphine, tri-(p-cyanophenyl)phosphine, tri-(p-nitrophenyl)phosphine, p-N,N-dimethylaminophenyl-(diphenyl)phosphine, and the like can be used if desired. Mixtures of triorganophosphorus compounds can also be used.

It will be recognized by one skilled in the art that other ligands used with rhodium for hydroformylation can, in turn, be used in the present invention for the hydroformylation of multicomponent syngas, provided the catalyst is used at sufficient ligand/Rh ratio. Further examples of ligands for hydroformylation include transition metal bis-phosphite catalysts (as disclosed in US 4,885,401), bidentate organophosphorus ligands (as disclosed in US 4,742,178), and transition metal polyphosphite ligands (as disclosed in US 4,769,498).

It will be further recognized by one skilled in the art that reaction media other than oily ones can be used in the present invention for the hydroformylation of multicomponent syngas. Typically, the catalyst is rendered soluble in a reaction medium by using suitable ligands for complexation. Thus the hydroformylation of MCS can be performed in aqueous media by using organophosphorus ligands containing at least one substituent on the hydrocarbon radical of the ligand which imparts water solubility to the ligand. Such subtituents include, for example, the carboxylic, amino, and sulfo functional groups. Examples of such ligands can be found in US patents 4,248,802, 4,808,756, 5,312,951, and 5,347,045 which are incorporated herein by reference. Hydroformylation of MCS can also be performed in a fluorinated hydrocarbon medium providing that the Rh complex is rendered fluorous soluble as described in US patent 5,463,082 which is incorporated herein by reference.

Rhodium complexes prepared using the aforementioned ligands may also be used in solution in the multiunsaturates removing absorber/regenerator system described previously. In fact using the spent catalyst solution from the hydroformylation reactor before its final disposal and/or recycle could be advantageous because of the potential savings in reagent cost in the multiunsaturates removing step.

Rhodium complex catalysts prepared using the aforementioned ligands are known to provide good catalytic activity in the hydroformylation of pure olefin feeds but are inhibited/poisoned by alkynes, particularly acetylene. Applicants, however, have unexpectedly found that these ligands can be used in the hydroformylation of syngas containing mixed C_2 to C_5 olefin and alkyne feed stocks, especially acetylene and ethylene, provided that the phosphorus and rhodium in the catalyst are present in amounts that render the catalyst

catalytically active. Preferably, the P/Rh ratio is maintained above a specified minimum value. We have found that, for triphenylphosphine (PPh_3), this minimum value should preferably be 30. The preferred ligand concentration can also be expressed in terms of the minimum concentration of the coordinately active phosphorus [P] in the solution or in terms of a minimum $[P]/p_{CO}$ ratio in the reaction, wherein p_{CO} is the partial pressure of carbon monoxide in the gas phase. For PPh_3, [P] should preferably be above 0.01 mol/l, and the $[P]/p_{CO}$ ratio should preferably be above 0.1 mmol/l/kPa. The Rh concentration in the reaction mixture should be in the range from about $1x10^{-5}$ to about $1x10^{-2}$ mol/liter. This range of Rh concentrations corresponds to a Rh concentration in the range from about 1 to about 1000 ppm (by weight). In a more preferred embodiment the Rh should be present in the range of 50 to 750 ppm, based on the total weight of the solution. Within the above ranges, the choice of catalyst concentration can reflect engineering and economic considerations.

The hydroformylation of the oxo reactor feed is carried out by contacting the catalyst with the multicomponent syngas in a solution of the catalyst prepared with a solvent or a mixture of solvents. Oily solvents that can be used for the preparation of a catalyst solution used in the oxo/hydroformylation step are known in the art, and include aliphatic, and aromatic hydrocarbons (e.g., heptanes, cyclohexane, toluene, etc.), esters (e.g., dioctyl phthalate), ethers, and polyethers (e.g., tetrahydrofuran, and tetraglyme), aldehydes (e.g., propanal, butanal, etc.), the aldol condensation products of the oxo product aldehydes, the triorganophosphorus ligand itself (e.g., triphenylphosphine), etc.

For catalyst compositions outside of the specified ranges, particularly for catalysts with P/Rh ratios below the minimum value for a catalytically active hydroformylation catalyst (which for PPh_3 is 30), the catalyst has a significantly reduced activity. Preece and Smith (EP 0,233,759), for example, have investigated the hydroformylation of an acetylene containing multicomponent syngas mixture in the presence of PPh_3 modified $Rh_6(CO)_{12}$ catalyst. In spite of the fact that the feed gas contained high concentrations of the reactants (acetylene, ethylene, CO, and hydrogen with a ratio of 6:3:30:61, respectively), the catalyst solution contained high concentration of Rh (0.0108 mol/l), and PPh_3 (0.114 mol/l), and the total pressure was 0.91 MPa, the catalyst failed as evidenced by the fact that the total turnover, in the presence of acetylene was only 13 in 24 hours, giving a very low turnover frequency of $1.5x10^{-4}$ mol propanal/mol Rh/sec. Under those reported conditions the Rh catalyst has high activity in the hydroformylation of ethylene alone (C. K. Brown, and G. Wilkinson, Tetrahedron Letters 1969, 22, 1725). Besides the expected propanal, the product mixture also contained 1.1 mole% acetone not observed in hydroformylation product mixtures of ethylene. This effect of acetylene on the oxo conversion of ethylene is well documented in the

literature, and is the reason that acetylenes are referred to as "classical catalyst poisons" for the phosphine modified Rh catalysts (see B. Cornils, "Hydroformylation Oxo Synthesis, Roelen Reaction" in New Syntheses with Carbon Monoxide, ed. J. Falbe, Springer Verlag, New York, 1980, p. 73).

Applicants have found, however, that under proper conditions, particularly at specific, appropriate P/Rh ratios the inhibiting/poisoning effect of alkynes can not only be overcome but in fact the alkyne components themselves can be converted to the corresponding saturated aldehydes. These ratios are typically high. The catalyst used by applicants herein shows enhanced activity, and is not poisoned by C_2-C_5 alkynes such as acetylene but rather co-converts them with olefins to corresponding C_3-C_6 aldehydes, as evidenced by its high turnover frequency with feed streams containing acetylene, ethylene, CO, and hydrogen. Applicants have found that the catalyst system evidences changed activity with varying coordinatively active P concentrations and P/Rh ratios. Physical evidence of this change comes from experiments conducted with acetylene and ethylene containing multicomponent syngas feeds at 100 and 110 ^{o}C, and 0.8 and 2.2 MPa total pressures, respectively, with different PPh_3/Rh ratios (see Examples 1, and 2). When the PPh_3/Rh ratio was 9.3, essentially the same as in the experiment of Preece and Smith, albeit using a different Rh source, the final catalyst solution had a dark brown color but was orange when the PPh_3/Rh ratio was higher, e.g., 300. The brown color of the solution containing the catalyst with a P/Rh ratio of 9.3 evidenced that the catalyst decomposed. At 110 ^{o}C, and 2.2 MPa total pressure the total turnover with a PPh_3/Rh ratio of 9.3 was only 4.9 in 2 hours, while under milder conditions of 100 ^{o}C, and 0.8 MPa total pressure the total turnover was 221 in 45 minutes when the PPh_3/Rh ratio was 300. This later catalytic rate is in the range of the hydroformylation rate of propylene under otherwise identical conditions. The catalyst with a PPh_3/Rh ratio of 300 thus showed an average turnover frequency of 0.082 mol propanal/mol Rh/sec, while the catalyst with a PPh_3/Rh ratio of 9.3 gave an average turnover frequency of 6.8×10^{-4} mol propanal/mol Rh/sec, i.e. 120 times slower. Initial turnover frequencies as high as 2 mol propanal/mol Rh/sec have been achieved with the process of the present invention in the conversion of an MCS feed which contained 15.5 volume % ethylene, and 6.5 volume % acetylene using a PPh_3/Rh catalyst with a PPh_3/Rh ratio of 660, and above (see Example 3).

Thus, one embodiment of the present invention is that, for any organophosphorus compound used to modify rhodium for use in hydroformylation, there exists a catalyst P/Rh ratio sufficiently high to create an active catalyst for the hydroformylation of multicomponent syngas. While catalysts below this P/Rh ratio may provide a minimal level of turnover, as evidenced by the turnover frequency of 0.8×10^{-4} mol oxo/mol Rh/sec achieved with PPh_3 at a

P/Rh ratio of 9.3, a catalyst with utility would preferably be at P/Rh ratio sufficiently high as to provide activity of at least 10^{-2} mol oxo/mol Rh/sec

Other experiments carried out with multicomponent syngas mixtures in the presence of rhodium PPh_3 catalysts with P/Rh ratios of 100 or higher showed high selectivity for propanal of about 99.5 %, in a wide range of H_2/CO, and acetylene/ethylene ratios and temperatures, even at conversions as high as 99 %. The only other product detected was ethane. On the other hand it has been reported (T. Mise et al. Chem. Lett. 1982, (3), 401) that acetylene and ethylene containing multi-component syngas mixtures yield α,β-unsaturated ethyl ketones in the presence of unmodified Rh catalyst, where the P/Rh ratio is zero.

Applicants have found at PPh_3/Rh ratios of at least 30, and preferably above about 100, significant improvements in rate, conversion, and stability are achieved. For example, at PPh_3/Rh ratios above 30, initial rates of at least 0.04 mol/mol Rh/sec and conversions of at least 80% have been achieved with an orange-yellow catalyst color that indicates a stable catalyst. At these PPh_3/Rh ratios, the hydroformylation of acetylene and ethylene containing MCS mixtures is facilitated and also may stabilize the catalyst in a form that catalyzes hydroformylation in preference to the formation of other oxygenates, such as ketones, and esters.

The aforementioned effect, in which the hydroformylation of acetylene and ethylene containing MCS mixtures stabilizes the catalyst, can provide a strong incentive to add alkynes (especially acetylene) to olefins (especially ethylene) for hydroformylation. Under conditions suitable for hydroformylation of olefins with alkynes and other multiunsaturates, both the ligand and the alkyne have equilibria strongly biased toward binding to the rhodium. This greatly reduces the reservoir of rhodium that has insufficient ligation, which in turn reduces the rate of rhodium cluster formation, which cluster formation is the principal pathway of rhodium deactivation. Thus, as shown in Example 7, catalyst deactivation can be greatly reduced by the addition of a small amount of alkyne. As such, one preferred embodiment of the present invention is a process for hydroformylating olefins (particularly ethylene) in which a small amount of alkynes (particularly acetylene) and/or multiunsaturates are added sufficient to mitigate catalyst deactivation. A preferred alkyne addition level would be from about 10 ppm to about 10% on total unsaturate, more preferably from about 100 ppm to about 5% on total unsaturate. The addition of alkynes or multiunsaturates may provide sufficient advantage in terms of reduced deactivation and in terms of the higher severity conditions (e.g. temperature, olefin conversion, etc.) enabled by reduced deactivation, that this embodiment can be used to improve olefin (particularly ethylene) hydroformylation, wherein the alkynes or

multiunsaturates are present essentially for the purpose of mitigating deactivation, and wherein aldehyde yield from those alkynes or multiunsaturates may be inconsequential or insignificant

For ligands other than triphenylphosphine, the minimum ligand concentration may be different. When the catalyst is used to convert multicomponent syngas mixtures that contain alkynes, an important characteristic of the ligand is its ability to compete against the alkyne for binding with the rhodium. The active rhodium catalyst has a varying amount of bound ligand, but an average over the active states can be defined in terms of a net bound-phosphorus/rhodium ratio, R_B. For common hydroformylation catalysts, R_B changes over time in the catalytic cycle, but has an average value of approximately 2. If a ligand has a greater attraction to be bound to Rh, less ligand will need to be in solution in order to maintain the Rh in its preferred (R_B) state.

A measure of the level of attraction of the ligand for the rhodium can be found in the pKa value of the ligand. (pKa values for some common ligands are listed in B. Cornils, "Hydroformylation Oxo Synthesis, Roelen Reaction" in New Syntheses with Carbon Monoxide, ed. J. Falbe, Springer Verlag, New York, 1980, p. 48). pKa is the base-10 logarithm of K_a, which is the equilibrium constant for the acid-base interactions of the ligand. A second measure of the level of attraction of the ligand for the rhodium can be drawn from the entropy of interaction when multi-dentate ligands are used. This entropy of interaction, ΔS_B, has a value of about 35 cal/mole/°K for each added point of attachment (see, for example, Benson, S. W. Thermochemical Kinetics, Wiley, New York, 1976). This entropy contributes to free-energy as -TAS, thus providing a free energy contribution of about -10 to -15 kcal/mole. Free energy influences equilibria as $\exp(-\Delta G/RT)$, such that the influence of entropy effect of multidentate ligands is included as $\exp(\Delta S_B/R)$.

Both measures of strength of binding will attenuate the concentration of unattached ligand that is required in solution in order to maintain an active amount of ligand bound to the rhodium. R_L is defined as the overall ratio of phosphorus to rhodium for a hydroformylation catalyst with ligand "L", and includes both unattached ligand and ligand bound to rhodium. The unattached ligand concentration (expressed as a ratio to rhodium concentration) is (R_L - R_B). The following equation defines the effect of binding strength parameters on the minimum ligand concentration for ligands other than PPh_3:

$$\frac{R_L - R_B}{R_{TPP} - R_B} = \frac{10^{(pKa_{TPP} - pKa_L)}}{e^{(\Delta S_B / R)}}$$

Where R_L is the minimum P/Rh ratio sufficient to provide an active hydroformylation catalyst with this ligand. R_{TPP} is the minimum P/Rh ratio for the ligand PPh_3 (R_{TPP}=30), R_B is the average ratio of P bound to the rhodium (~2), pKa_{TPP} is the pKa value for PPh_3, pKa_L is the pKa value for the new ligand, ΔS_B is about 35 kcal/mole/°K for each additional point of attachment (beyond the one point of attachment of PPh_3), and R is the gas constant (1.99 cal/mole/°K)

Thus, R_L, as calculated using this equation, represents the minimum P/Rh ratio sufficient to provide an active hydroformylation catalyst for any ligand "L"

Rhodium can be introduced into the reactor by methods known in the art either as a preformed catalyst, for example, a solution of hydridocarbonyl tris(triphenylphosphino) rhodium (I) [$HRh(CO)(PPh_3)_3$] or formed in situ. If the catalyst is formed in situ, the Rh can be introduced as a precursor such as acetylacetonatodicarbonyl rhodium (I) [$Rh(CO)_2(acac)$], rhodium oxide [Rh_2O_3], rhodium carbonyls [e.g., $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$], tris(acetylacetonato) rhodium (I) [$Rh(acac)_3$], or triarylphosphine substituted rhodium carbonyls {[$Rh(CO)_2(PAr_3)$]$_2$, wherein Ar is an aryl group}

REACTOR VARIABLES

Typically, in the process of the present invention, hydroformylation of multicomponent syngas feeds is conducted at a temperature in the range from 80 to 180 °C, and preferably in the range from 80 to 155 °C. If the temperature exceeds these limits, the catalyst may rapidly deactivate. Lower temperatures are acceptable, however, the rate of reaction may become too slow to be economically practical

The reaction is conducted at a total pressure in the reactor in the range of less than about 5 MPa (absolute) preferably about 0.05 to 5 MPa with a partial pressure of carbon monoxide not greater than 50 % of the total pressure. The maximum practical pressure can be limited by considerations of production and capital costs, and safety

The mole percent of carbon monoxide, hydrogen, C_2-C_8 olefins, preferably ethylene, and C_2-C_8 alkynes, preferably acetylene in the multicomponent syngas feed to the oxo reactor

at the foregoing pressures should be maintained as follows: CO from about 1 to 50 mol%, preferably about 1 to 35 mol%; H_2 from about 1 to 98 mol%, preferably about 10 to 90 mol%; monounsaturates individually and in combination from about 0.1 to 35 mol%, preferably about 1 to 35 mol%. Gas compositions within the oxo reactor in the process of the present invention are then affected by the mode of operation, feed composition, and conversion.

The reaction can be conducted either in a batch mode or on a continuous basis. Preferably the reaction is run on a continuous basis. In a continuous mode, superficial velocities of from about 1.5 to about 61 cm/sec (0.05 to 2 ft/sec), preferably from about 3 to about 30 cm/sec (0.1 to 1 ft/sec) should be used.

Since the catalytic oxo conversion takes place in the liquid phase and the reactants are gaseous compounds, high contact surface between the gas and liquid phases is very desirable in order to avoid mass transfer limitations. The high contact surface can be provided by any suitable manner, for example, by stirring in a batch reactor operation. In a continuous operation the reactor feed gas can be contacted with the catalyst solution in, for example, a continuous stirred tank reactor in which the gas is introduced and dispersed at the bottom of the vessel. Good contact between the catalyst and the gas feed can also be ensured by dispersing the solution of the Rh complex catalyst on a high surface support by methods recognized in the art.

In the process of the present invention the hydroformylation of multi-component oxo reactor feeds can be conducted in a single-stage reactor or using multiple reactors. The reactors may be arranged in any numbers of parallel trains when operating in a continuous mode. The number of parallel trains is determined by the desired total capacity and the capacity of a single train. The present invention can be practiced using one or more stages per train, and each reaction stage can be engineered using any suitable reactor configuration. For example, plug flow or constant stirred tank reactor (CSTR) contacting are two common reactor configurations. The number of stages and the reactor types for the stages can be computed using conventional chemical engineering principals given the kinetics and objectives of the reaction system.

In batch experiments, there is an indication that the olefin and alkyne components of MCS feeds react in two well defined phases. The first phase roughly corresponds to the conversion of the olefins present in the MCS oxo reactor feed. In the second phase on the other hand mostly the alkyne content is converted. The first phase is essentially the

hydroformylation of olefins in the presence of alkynes. The second phase on the other hand itself is a two step conversion in which alkynes are first hydrogenated to olefins and then those olefins formed are hydroformylated to the corresponding aldehydes. The rate determining step in this second phase of MCS conversion is the hydrogenation of alkynes to olefins. Following this unexpected order and complexity of the oxo conversion of mixed olefin-alkyne feeds, conditions for the different phases of the oxo reaction are preferably different. Thus, a preferred embodiment of the present invention is to divide the total hydroformylation into two stages, with each stage operated under conditions advantageous to the chemistry occurring in that stage. Thus reaction conditions and catalyst composition in the first reactor should enhance the hydroformylation of olefins in the presence of alkynes. Reaction conditions and catalyst composition in the second stage, on the other hand, should facilitate the hydrogenation of alkynes which is the slowest step in their conversion to aldehydes.

US Patent 4,593,127 describes a two stage hydroformylation process for the oxo conversion of olefins. The patent gives a common engineering solution for an improvement in the overall conversion of the reactant olefins. It has to be understood, however, that the purpose and need for a multi-stage and in particular for a two stage oxo conversion in the process of the present invention is different. The chemical reactions taking place in the different stages of the oxo process of the present invention are different. In the first oxo stage the main reaction is the hydroformylation of olefins in the presence of alkynes. In the second stage, however, the main reaction is the hydroformylation of alkynes which is itself a two stage reaction. The first step in the alkyne conversion is the hydrogenation of alkynes to the corresponding olefins which is followed by the hydroformylation of the formed olefins to the corresponding aldehydes. The chemical reaction in the two stages of the process disclosed in US Patent 4,593,127 on the other hand is the same: hydroformylation of olefins to aldehydes. The need for the two stages in the process of the present invention therefore does not simply stem from the need for a better overall conversion but from the unexpected nature of the chemical process, namely, that the stronger binding alkyne components react much slower than the weaker binding olefin components. As a result of this characteristics of the oxo conversion of alkyne-olefin mixtures, olefins react first producing the corresponding aldehydes and thus the alkyne reactants will be enriched in the reaction mixture. Furthermore, since the oxo conversion of alkynes to the final saturated aldehyde products requires first the hydrogenation of alkynes to the corresponding olefins and since it is this first step which determines the overall rate of this reaction, conditions in the second reactor stage should enhance in fact not only the hydroformylation of olefins but the hydrogenation of alkynes as well. The need for the second reactor stage therefore stems from the nature of the chemistry

and not simply a common engineering solution to improve of the overall conversion of a chemical process.

An example of a two-stage, single-train oxo/hydroformylation unit is shown in Figure 2 and described as follows: The hydroformylation reaction is carried out in two continuous stirred tank reactors (21, 23). Each reactor is cooled and stirred using a pump-around cooling loop (202, 207). The hydroformylation feed (201) enters the first reactor. The product from the first reactor (203), possible containing some entrained solvent and/or catalyst, may be cooled and separated in a flash drum (22) for intermediate withdrawal of aldehyde product (204). Remaining (unconverted) multicomponent syngas (205) is introduced into the second reactor (23). Additional MCS components, such as hydrogen, can be added (206) to this MCS feed to the second reactor. Hydrogen addition, for example, could be employed to provide the higher H_2/CO ratios that are preferred in the second stage. The product from the second reactor (208) is combined with the intermediate product (204) to yield a stream (209) that is introduced to a product separation and catalyst recovery train (combined for simplicity into block 24). This block can use conventional boiling-point based separations (e.g. distillation) to separate the crude product into an unconverted MCS stream (210), a purified aldehyde stream (211), and a process solvent/catalyst stream (212). The process solvent and catalyst stream (212) is recycled back to the individual reactor stages.

Conditions in a two-stage oxo unit embodiment of the process of the present invention are adjusted for the two stages of the conversion of multicomponent syngas feeds as described previously. Therefore, in the preferred embodiment reaction conditions in the first stage of the two-stage oxo unit should be optimized to facilitate hydroformylation of ethylene in the presence of acetylene. In the second stage of the conversion process the overall conversion rate is essentially determined by the rate of hydrogenation of alkynes, in the preferred embodiment acetylene. Thus, reaction conditions in the second stage of a two-stage oxo unit should facilitate hydrogenation of the alkyne reactant, in the preferred embodiment acetylene. Reaction conditions in the first stage should be maintained as follows: H_2/CO ratio from about 1:1 to 100:1, preferably 1:1 to 10:1, the temperature should be from about 80 to 180 °C, preferably in the range of 80 to 155 °C, more preferably from about 80 to 130 °C, the total pressure in the reactor should be from about 0.05 to 5 MPa, preferably from about 0.1 to 2.5 MPa, with a partial pressure of CO not greater than 50 % of the total pressure, and the partial pressure of acetylene reactant not greater than 0.2 MPa (safety limit). Reaction conditions in the second stage of a two-stage oxo unit of the process of the present invention should facilitate the hydrogenation of alkynes to olefins by, for example, maintaining higher H_2 and lower CO partial pressures than in the first stage. Higher temperatures may also be

applied in the second stage to increase reaction rates. In some cases it may become economically advantageous to use a different ligand in the second stage to improve the heat stability and/or hydrogenation activity of the catalyst. Thus reaction conditions in the second stage should be maintained as follows: H_2/CO ratio from about 1:1 to 100:1, preferably from about 2:1 to 50:1; the temperature should be maintained between about 80 to 180 ^oC, preferably from about 80 to 155 ^oC; the total pressure should be maintained between about 0.05 to 5 MPa, preferably from about 0.1 to 2.5 MPa, with a partial pressure of CO not greater than 35 % of the total pressure, and the partial pressure of acetylene not greater than 0.2 MPa (safety limit). Superficial velocities of from about 1.5 to about 61 cm/sec (0.05 to 2 ft/sec), preferably from about 3 to about 30 cm/sec (0.1 to 1 ft/sec) should be used in both reactors in order to entrain the catalyst in the reactor. Rhodium complex catalysts within the range of compositions disclosed previously are used. The compositions of the catalyst solutions in each stage of a multistage oxo unit are preferably the same, but can also be different, within the disclosed ranges for the rhodium complex catalyst, if so desired

The overall conversion of the alkyne and olefin content of the multicomponent syngas feed in the oxo unit of the process of present invention can be essentially as high as desired. The catalyst life, however, is shortened as the conversion approaches 100% in a single pass if higher catalyst concentrations and/or more severe conditions, i.e. higher temperatures are used to reduce the necessary residence time to achieve the desired conversion. It is therefore generally desirable to maintain the conversion in a single pass lower than the desired overall conversion and to recycle the reactants after the separation of the product. Thus, for example, higher than 99% overall conversion can be achieved with 80% per pass reactant conversion in the oxo unit and 96% reactant recovery in a recovery-recycle unit described below. Under such conditions the reactant concentration in the reactor can be 24 times higher than the concentration resulting from the same level (99%) of single pass conversion in the absence of recycle. This higher concentration contributes to a proportionally 24 times higher reaction rate, and in the case of the oxo/hydroformylation process of the present invention, it also contributes to an increased catalyst complex stability.

REACTANT RECOVERY AND RECYCLE

The use of a recycle of unreacted unsaturated hydrocarbon components is highly desirable in the processes of the present invention to increase the oxo unit productivity and the catalyst life by allowing higher unsaturated hydrocarbon concentrations in the oxo reactor(s). However, feeds having relatively high concentrations of inerts and non-stoichiometric reactants, such as multicomponent syngas feeds, effectively discourage such a recycle because

of the rapid build-up of excess gaseous materials, i.e. inerts (e.g., nitrogen, water vapor, methane, ethane, propane), and excess reactants (typically hydrogen) that would occur in the recycle loop. It would be beneficial if a process could be devised to overcome these problems.

Applicants have found that the unreacted unsaturated hydrocarbon components, especially acetylene, can be advantageously recovered from the gaseous effluent of the oxo reactor by scrubbing this "tail gas" with a liquid consisting of the liquid aldehyde product of the oxo reactor. This unsaturates-containing liquid can then either be stripped with unsaturates-free syngas to produce a recycle stream of multicomponent syngas that is more concentrated in the unsaturated hydrocarbon than was the tail gas, or preferably, the unsaturates-containing liquid can be recycled directly to the oxo reactor

Applicants have found that solubilities of the unsaturated hydrocarbon components (e.g., ethylene, and in particular acetylene) of multicomponent syngas mixtures in certain oxygenated solvents, more particularly C_3-C_6 oxygenated solvents, especially the product aldehyde of the hydroformylation process such as disclosed herein for the conversion of multicomponent syngas mixtures are exceptionally high. Furthermore, the solubilities of these unsaturated hydrocarbons are substantially higher than the solubilities of other reactants such as hydrogen, and carbon monoxide, and inerts such as methane, and nitrogen (see Tables 6 and 7 in Example 5) present in multicomponent syngas mixtures used in the process of the present invention

Thus, another embodiment of the present invention provides a process for the separation or preferential removal of unsaturated hydrocarbons, especially acetylene, from oxo reactor effluents containing same and recycle thereof into the oxo reactor for further hydroformylation processing without build-up of the aforementioned excess reactants and inerts in the oxo reactor. The process provides a method for concentrating and recovering the unsaturated hydrocarbons from the oxo reactor effluent to produce a stream that is enriched in alkyne and olefin and deficient in excess gaseous material for recycle into the oxo unit without buildup of inerts, and excess components

The recycle and recovery concept of the present invention comprises use of the aldehyde product of hydroformylation as the absorption solvent in a system for concentrating the unconverted unsaturates in the oxo reactor effluent. A simple embodiment of this invention would be the use of paired absorption and stripping towers. In this method, the oxo effluent is fed to the bottom of an absorption tower where it is contacted with cold aldehyde

to condense out liquid aldehyde and dissolve unsaturated species (particularly acetylene). Oxo tail gas greatly diminished in these components emerges from the top of the absorption tower. The unsaturates-containing aldehyde from the bottom of the absorption tower is fed to the top of a stripping tower wherein unsaturates-free gas (such as synthesis gas, hydrogen, or nitrogen) is used to strip out the unsaturates into a concentrated vapor phase suitable for recycle to oxo. The unsaturates-free liquid aldehyde product at the bottom of the stripper is divided between recycle to the absorber and a stream which is the aldehyde product of oxo. By use of such a scheme, the absorber/stripper is made to serve the three purposes: (i) recovering the aldehyde product from the gaseous process effluent, (ii) recovering unsaturates for recycle to oxo, and (iii) removal of unsaturates from the aldehyde product, in which such unsaturates would be unwanted contaminants.

A preferred embodiment of the recycle and recovery concept of the present invention accomplishes these same three purposes, but also provides for the recycle of the unsaturated components as solutes in a liquid-phase recycle aldehyde stream. An example flow diagram for this embodiment is shown in Figure 3. Into the oxo reactor (31), having a pump-around cooling loop (340), is introduced a multicomponent syngas feed (331). The oxo reactor gaseous or mixed phase effluent (332) is cooled to a temperature at which an amount of aldehyde condenses that is essentially equal to the amount of oxo-produced aldehyde. The condensed liquid aldehyde (341) is separated from the remaining gas phase oxo effluent in a flash drum (33). The liquid aldehyde product (341) is introduced into a stripping vessel (34) where it is stripped with an unsaturate-free gas (333) (e.g. syngas, hydrogen, nitrogen, or light alkanes) to produce an unsaturate-free aldehyde product (335) and a gaseous effluent (342) containing unsaturated hydrocarbons. The stripping tower gaseous effluent (342) is combined with the flash drum (33) vapor and cooled further to produce a stream (334) that is fed to the absorption tower (35) having an upper portion that is at a temperature sufficiently low to provide reflux (344) of the alkane components of the oxo effluent (e.g. ethane or propane), as shown as cooling of the tower overhead (343) and drum (36) to separate liquid from vapor. This upper portion of the absorber (35) functions as the rectifying section of a distillation tower, rejecting aldehyde from lower boiling components, and resulting in a substantially aldehyde-free overhead product stream (336) that contains the oxo diluents (e.g. N_2, methane, ethane, propane) and non-stoichiometric components (e.g. hydrogen) that boil at temperatures at or below the temperature of the refluxing alkane. In the bottom of the tower (35) the liquid phase becomes cold aldehyde that dissolves the highly soluble unsaturated components as if in an absorber. At the temperature of the bottom of the tower (35) the solubilities of alkynes and olefins in the liquid phase are very high (see Tables 5 and 6 in Example 5). For example, acetylene concentrations of 10 mol% can be achieved in the

acetylene rich aldehyde product at appropriate conditions. This unsaturates-containing liquid stream (337) emerges from the bottom of the tower where it can be pumped as a liquid to substantially higher pressures for recycle to the oxo reactor (31). Once at higher pressure, the unsaturates-containing liquid stream can be heat exchanged (350) to recover any cooling value that it might contain. In this high pressure condition this heat exchange can be accomplished with a minimized concern that unsaturates such as acetylene will separate from the liquid to form a dangerous concentrated phase. Recovery of cooling value can also be employed on other cooled streams (335, 336) exiting the process.

In a further variation on this scheme, the pressure of the oxo effluent (332) can be increased in pressure prior to the recovery process via a compressor (32). The pressure increase should not increase the partial pressure of the product aldehyde over its saturation limit in order to avoid compressor damage. Furthermore, the partial pressure of acetylene at the high pressure side should be lower than the safety limit of 0.2 MPa. The increased pressure typically should not be higher than 5 MPa in order to avoid excessive equipment cost. Such a pressure increase results in an increase of the partial pressures of the components being separated: the product aldehyde and the unconverted C_2 to C_5 monounsaturates. As a result of the higher partial pressures the flash tower 33, and scrubber 35 may be operated at higher temperatures thus potentially reducing the cooling cost of the separation. Furthermore, increasing pressure can carry the added advantage of reducing tower sizes for gas treating and separations. The need and degree of this operational compression step is determined by economic and safety factors.

This recycle and recovery process is entirely different from that described in US Patent 3,455,091 in several ways. First, US Patent 3,455,091 uses high boiling oxo side-products as scrubbing solvents, versus our preferred use of the primary oxo product. Second, US Patent 3,455,091 uses the scrubbing system to absorb for recovery purposes the primary-product aldehyde out of the unconverted oxo feed gases, versus our absorption for recycle to oxo of selected unconverted feed components out of other feed components. This recycle and recovery process is also entirely different from that described in US Patent 5,001,274. While US Patent 5,001,274 employs a rhodium catalyst stream to absorb for recycle selected unconverted feed components, the process described herein uses the liquid reaction product. A further difference between the process of the present invention and the aforementioned prior art is that the processed stream is not the effluent of an olefin oxo unit but in fact the effluent of a different oxo technology in which olefins and alkynes are co-converted. The processed stream therefore contains chemically different components - C_2 to C_5 alkynes - in high concentration, the treatment and recovery of which requires special process conditions

and technology (safety). One of the most important features of the recovery-recycle process of the present invention is that it provides a solution for the safe recovery and recycle of those alkynes, especially of acetylene.

It should be noted that this recycle and recovery process may be used with processes other than the aforementioned and herein described hydroformylation/oxo processes. The recovery and recycle process disclosed herein may be used with other synthesis processes whose reaction products are usable as absorption solvents for unreacted gaseous feed components and which synthesis process is not harmed by the recycle of said products back to the synthesis reactor. For example certain implementations of Fischer-Tropsch ("FT") synthesis can be made to produce oxygenates as products and to consume olefins in the synthesis gas feed. In such an implementation, the FT oxygenate product can be used as described herein to recover and recycle unconverted olefinic species back to the synthesis reactor. Another example is the variations of alcohol synthesis reactions that consume olefins in the synthesis gas feed and produce higher alcohol products. These are only examples and should not limit in any way the scope of application of the basic concept.

The solvent applied in the unsaturates recovery-recycle process, as it is applied to hydroformylation of multicomponent syngas, is the recovered aldehyde product from the hydroformylation of multicomponent syngas containing C_2-C_5 monounsaturates. Use of the product aldehyde as a solvent presents several advantages: the separation of the product aldehyde can be integrated into the unsaturates recovery and recycle process saving capital cost, there is reduced need for purchased solvent and solvent make-up, and reduced product contamination and solvent/product separation problems. An integrated product separation and unsaturates recovery and recycling scheme can offer further advantages relating to the need of use of refrigeration for the effective separation of the product aldehyde. Since both product separation and unsaturates recovery requires the application of low temperatures, the cooling energy can be efficiently utilized in an integrated process such as disclosed herein.

PRODUCT UTILIZATION

C_3 to C_6 aldehydes, which are a desired product of the hydroformylation stage of the present invention, and particularly propanal, have utility as intermediates in the manufacture of many industrial commodity chemicals. Thus, one preferred embodiment of the present invention is its combination with subsequent processing steps that further enhances the value of the aldehyde product.

One preferred embodiment of the present invention is the combination of the hydroformylation of a multicomponent syngas with hydrogenation of the aldehyde product of that hydroformylation to produce an alcohol product. Particularly preferred is the production of propanol by this means. An additional preferred embodiment of the present invention is the combination of the hydroformylation of a multicomponent syngas with the oxidation of the aldehyde product of that hydroformylation to produce an organic acid product. Particularly preferred is the production of propionic acid by this means. Hydrogenation and oxidation of the aldehyde to the aforementioned products may be carried out according to procedures known in the art.

An additional preferred embodiment of the present invention is the combination of the hydroformylation of a multicomponent syngas with an aldol condensation step. Aldol condensation is a conversion step that is well known in the art. In this reaction, two aldehydes are joined such that the α-carbon of the first becomes attached to the carbonyl carbon of the second. The result is called an "aldol", which is a β-hydroxy carbonyl compound. Typically, the aldol eliminates H_2O to yield an unsaturated aldehyde. The aldol condensation of two identical aldehydes is called "self-aldol", while the aldol condensation of two different aldehydes is called "cross-aldol". Additional preferred embodiments of this invention include the hydrogenation of so-produced aldols to saturated aldehydes, as well as saturated and unsaturated alcohols. An additional preferred embodiment of this invention is the oxidation of the saturated and unsaturated aldehydes derived from the aldol condensation to corresponding saturated and unsaturated acids.

Thus, an additional preferred embodiment of the present invention is the combination of the hydroformylation of a multicomponent syngas with self-aldol of the produced aldehyde to produce an aldol dimer. Particularly preferred is the production of 2-methylpentenal by this means, and the subsequent hydrogenation to 2-methylpentanal, and/or to 2-methylpentanol, as well as the oxidation of the 2-methylpentanal to 2-methylpentanoic acid.

An additional preferred embodiment of the present invention is production of multi-methylol alkanes via the cross aldol condensation of formaldehyde with of the aldehydes produced by the hydroformylation of a multicomponent syngas. A further preferred embodiment of the present invention is production of multi-methylol alkanes via cross aldol condensation of formaldehyde with the unsaturated or saturated (hydrogenated) aldehydes produced as aldol-dimers of the aldehydes produced via hydroformylation of a multicomponent syngas. Typically in this known art, the carbonyl (C=O) group in such a

cross-aldol product is chemically or catalytically reduced such that all the oxygen of the multi-methylol alkane is in the hydroxyl form. Particularly preferred are the production of trimethylol ethane by this means (by cross-aldol of formaldehyde with propanal), and the production of 2,2'-dimethylol pentane by this means (by cross-aldol of formaldehyde with 2-methylpentanal). Conversion of aldehydes to the aforementioned products may be carried out according to procedures known in the art.

Thus, the present invention includes a process for the manufacture of alcohols, wherein the aldehydes formed by the hydroformylation of a multicomponent syngas are hydrogenated to form the corresponding alcohols; a process for the manufacture of acids, wherein the aldehydes formed by the hydroformylation of a multicomponent syngas are oxidized to form the corresponding acids; a process for the manufacture of aldol dimers, wherein the aldehydes formed by the hydroformylation of a multicomponent syngas are self-aldolized to form the corresponding dimers; a process for the manufacture of saturated aldehydes, wherein those aldol dimers are hydrogenated to corresponding saturated aldehydes; a process for the manufacture of unsaturated alcohols or acids, wherein the aldol-dimers are hydrogenated or oxidized to form the corresponding unsaturated alcohols or acids; a process for the manufacture of saturated alcohols, wherein the aldol-dimers are hydrogenated to form the corresponding saturated alcohols, a process for the manufacture of saturated alcohols or acids, wherein the saturated aldehydes produced via hydrogenation of the aldol-dimers are hydrogenated or oxidized to form the corresponding saturated alcohols or acids, a process for the manufacture of multi-methylol alkanes, wherein the aldehydes formed by the hydroformylation of a multicomponent syngas are aldol-condensed with formaldehyde to form the corresponding multi-methylol alkanes, a process for the manufacture of trimethylol ethane, wherein propanal that is formed by the hydroformylation of a multicomponent syngas is aldol condensed with formaldehyde to form the trimethylol ethane, and a process for the manufacture of multi-methylol alkanes, wherein the aldol-dimers and/or the saturated aldehydes produced therefrom are aldol-condensed with formaldehyde to form the corresponding multi-methylol alkanes.

This invention can be used to produce the propanal-containing composition that is used for the production of aldehydes, alcohols, acids, and their derivatives, described in EPA 95.300 301.9 and the PCT application based thereon, which are hereby incorporated by reference.

Example 1

Apparatus

Experiments were carried out in an Autoclave Engineers' 300 ml stainless steel autoclave. The reactor was connected to a 500 ml high pressure buffer bomb through a regulator valve. Both the reactor and the buffer bomb were equipped with digital temperature and pressure gauges. The autoclave was also equipped with a temperature control unit, and a stirrer with speed control. The total and free volumes of the different parts of the apparatus were measured by gas volumetric method.

Catalyst preparation

The rhodium and phosphine containing solutions were prepared in Vacuum Atmospheres dry boxes under nitrogen or argon. The rhodium was charged either in the form of $HRh(CO)(PPh_3)_3$, or as $Rh(CO)_2(acac)$, where PPh_3 is triphenylphosphine, and acac is the acetylacetonato ligand. $Rh(CO)_2(acac)$ was purchased from Strem Chemicals and was used as received. $HRh(CO)(PPh_3)_3$ was prepared from $Rh(CO)_2(acac)$ by literature method (G. W. Parshall, Inorg. Synth. 1974, 15, 59). Toluene was distilled from sodium benzophenone under nitrogen. The weight of each component of the toluene solution was measured. Methylcyclohexane was used as an internal GC standard. The solution was charged under flow of nitrogen into the autoclave. The unit then was flushed with syngas (H_2/CO = 1). When the catalyst was prepared in situ the autoclave was pressurized to about 0.5 MPa at room temperature then it was heated up to 100 °C, and was kept at that temperature for about 30 min. Independent experiments demonstrated that under these conditions the rhodium looses the acac ligand by hydrogenation and the formed hydridocarbonyl triphenylphosphino rhodium complex(es) ($HRh(CO)_x(PPh_3)_y$, $x+y = 4$) catalyze hydroformylation without showing any induction period. When $HRh(CO)(PPh_3)_3$ was used as a Rh source no catalyst preforming was necessary.

Hydroformylation of Gas Blend #1

The reactor containing the solution of the preformed catalyst was flushed and pressurized with Gas Blend #1 containing ethylene, ethane, acetylene, carbon dioxide, hydrogen, methane, carbon monoxide, and nitrogen (composition is given in Table 2) at room temperature. The amount of gas loaded into the reactor was determined by gas volumetric method. The P/Rh ratio in this experiment was 9.3. The composition of the catalyst charged is given in the footnote of Table 2. The reactor was heated to 110 °C and maintained at

reaction temperature for two hours. While the reactor was at the reaction temperature, a pressure drop indicated that reaction occurred. After two hours at 110 °C, when no further pressure drop was observed, the reactor was chilled to 15 °C, and gas and liquid samples were taken. A mass balance was established for the charged materials based on gas chromatography (GC) analyses of the gas and liquid phases. The results are given in Table 2. In the liquid phase the only detected product of the reaction was identified by gas chromatography/mass spectrometry (GC/MS) as propanal. The propanal found in the liquid phase gave a 60 % conversion based on the total amount of ethylene and acetylene loaded into the reactor. Since the experiment was stopped when the oxo reaction ceased the catalyst clearly deactivated before higher conversions could have been achieved. Gas analysis of the final reaction mixture indicated that both unreacted ethylene and acetylene were present at a ratio of acetylene/ethylene of 3.4 at the point when the oxo conversion stopped. The analysis results showed that a parallel conversion of both ethylene and acetylene had occurred. The final solution had a dark brown color which is associated in the experiments disclosed herein with a decomposed catalyst.

Table 2. Hydroformylation of Multicomponent Syngas (Gas Blend #1) at 110 °C

Compound	x^o (v.%)	n^o (mmol)	n^f (mmol)	Δn (mmol)
C_2H_4	1.020	1.9	0.5	-1.4
C_2H_6	0.105	0.2	0.2	0.0
C_2H_2	2.910	5.4	1.7	-3.7
CO_2	1.650	3.1	2.4	-0.7
H_2	22.310	41.6	25.5	-16.1
CH_4	4.990	9.3	8.9	-0.4
CO	11.120	20.8	15.8	-5.0
N_2	55.895	116.0	121.6	+5.6
Propanal*	--	--	4.4	+4.4
Total	100.000	198.3	184.0	-17.3

Reaction conditions: toluene 90 ml, methyl cyclohexane (internal standard for GC) 0.8 ml, Rh 897 µmoles (1130 ppm), PPh_3 8.3 mmoles, p^o 1545 kPa (at 20 °C), reaction time at 110 °C 2 hrs.

Legend: x^o = initial gas concentration, n^o = initial number of mmoles in the gas phase, n^f = final number of mmoles in the gas phase, Δn = mole number change in the gas phase.

* Liquid GC results

Example 2

The apparatus, catalyst preparation method, and experimental procedures were the same as in Example 1. Gas Blend #2, used in this experiment, contained ethylene, ethane, acetylene, carbon dioxide, hydrogen, methane, and carbon monoxide (the composition is given in Table 3). The reaction temperature was 100 °C, and the P/Rh ratio was 300. The composition of the catalyst solution is given in Table 3. After heating the reaction mixture to 100 °C, a fast pressure drop in the autoclave was observed indicating that a gas consuming reaction took place. This pressure drop significantly slowed down after about 45 min reaction time when the reaction was stopped by cooling the reaction mixture to 15 °C. After cooling the system gas and liquid samples were taken, and analyzed by GC. The results are given in Table 3. The analyses of both the gas and liquid phases gave a higher conversion (88.5 %) at a 10 °C lower temperature, 14 times lower catalyst concentration, and in a 2.7 times shorter time than what was observed in Example 1. In addition, the color of the solution sample taken at the end of the experiment was bright orange yellow. An orange yellow color in the herein discussed experiments is associated with an active catalyst system in the conversion of acetylene and ethylene containing multi-component syngas mixtures

Table 3. Hydroformylation of Multicomponent Syngas (Gas Blend #2) at 100 °C

Compound	x^o (v. %)	n^o (mmol)	n^f (mmol)	Δn (mmol)
C_2H_4	9.91	9.49	0.77	-8.72
C_2H_6	3.26	3.12	1.69	-1.43
C_2H_2	6.83	6.54	1.08	-5.46
CO_2	2.53	2.42	1.51	-0.91
H_2	48.27	53.09	47.17	-5.92
CH_4	11.70	11.21	9.14	-2.07
CO	17.50	23.32	8.65	-14.67
Propanal*	--	--	14.20	+14.20
Total	100.00	109.19	84.21	-24.98

* Liquid GC result

Reaction conditions: toluene 60 ml, methyl cyclohexane (internal standard for GC) 0.8 ml, Rh: 64.3 μmoles (110 ppm), PPh_3 19.3 mmoles; p^o = 800 kPa (at 100 °C), reaction time at 100 °C: 45 min.

Legend: x^o = initial gas concentration, n^o = initial number of mmoles in the gas phase, n^f = final number of mmoles in the gas phase, Δn = mole number change in the gas phase.

Example 3

This example demonstrates the effect of P/Rh ratio on the hydroformylation of acetylene and ethylene containing MCS oxo feed streams. The preparation and loading procedures of the catalyst solutions were the same as in Example 1. The solvent, tetraethylene glycol dimethyl ether (tetraglyme), was degassed before use. It also served as an internal standard in the GC analyses of the product liquid samples. The solution volume, and the total initial gas charge in each experiment was the same, 70 ml, and 95 mmoles, respectively. The apparatus was the same as in Example 1 except that a volume calibrated, high pressure injection bomb was mounted into the feed line after the high precision pressure regulator between the buffer cylinder and the autoclave. This injection bomb was used to inject known amounts of ethylene/acetylene mixtures into the autoclave. The ethylene, and acetylene charges in each experiment were around 15.4, and 6.4, respectively.

Batch kinetic experiments were carried out at constant 1 MPa total gauge pressure and 120 ^{o}C. As the reaction proceeded a constant pressure was maintained by feeding syngas (CO/H_2 = 1) from the volume calibrated high pressure buffer bomb through a high precision regulator valve. The reaction was monitored by reading the pressures in the buffer (measured to an accuracy of 1 kPa) as a function of time (recorded to an accuracy of 1 second). The overall conversions of ethylene and acetylene were determined after each run by GC analyses of the liquid and gas products. The only two products of the reactions detected were propanal as major product and minor amounts of ethane. The overall conversion then was correlated to the total pressure drop and the total gas consumption in moles from the buffer bomb during the experiment. Reaction rates were calculated assuming a linear correlation between the pressure drops and conversion. Catalyst compositions, and results of seven different experiments are shown in Table 4.

Table 4. Effect of PPh_3 Concentration on the Oxo Reaction Rate and on the Conversion of Acetylene-Ethylene Mixed Feeds

PPh_3 (mmoles)	Rh (μmoles)	P/Rh	Initial Rate (mol/mol Rh/sec)	Total C_2 Conversion (%)
0.38	37.8	10	0.02	25
1.17	37.7	31	0.04	80
4.32	37.7	115	0.1	80
8.45	37.4	226	0.3	80
16.37	37.6	435	0.9	92
23.40	38.0	660	2.1	99
30.93	18.8	1644	2.1	99

Solution Volume: 70ml, H_2/CO = 1; Total Pressure = 1 MPa; Initial Gas Charge 95 mmoles total, 15.4 mmoles C_2H_4, 6.4 mmoles C_2H_2, balance CO and H_2, rhodium concentration is 54 ppm and 27 ppm for 38 and 19 μmoles, respectively

Kinetic data in Table 4 demonstrate that the activity of the catalyst increases significantly by increasing the phosphine concentration. The color of the final solutions were orange yellow, except for the run with PPh_3/Rh ratio of 10, which was brown after 120 min reaction time. This color variation indicates that a stable catalyst system is not present at a PPh_3/Rh ratio of 10 in the hydroformylation of acetylene and ethylene containing multi-component syngas feeds. Under the preferred PPh_3/Rh ratios above 30, significant improvement in rate, conversion, and stability are achieved.

Example 4

The example demonstrates the effect of H_2/CO ratio on alkene (ethylene) hydroformylation in the presence of a cumulated diene (allene). The preparation and loading procedures of catalyst solutions were the same as in Example 1. The experimental method and the kinetic evaluation of experimental values were the same as in Example 3, except that 15 mmoles of ethylene was coinjected with 0.13 mmoles of allene and with different amounts of hydrogen to adjust H_2/CO ratios in the autoclave. The catalyst charge was 18.8 μmoles of Rh (27.7 ppm), and 8.3 mmoles of PPh_3 (3.1 w %) in each experiment.

After injecting allene-ethylene mixtures into the autoclave at 120 °C the reaction first proceeded at a very slow rate. Gas analysis of the gas reaction mixture showed a slow build-up of propylene during this first slow stage of the reaction. The hydroformylation of ethylene took place only after essentially all (typically 95 to 99 %) of the allene charged was converted. The length of this first phase of the reaction depended on the H_2/CO ratio (see Table 5).

Table 5 The Effect of H_2/CO Ratio on the Conversion Rate of Allene

H_2/CO	Time Required to Convert Allene (min)	Reaction Rate (mol C_3H_4/mol Rh/min)
1.0	23	0.30
2.2	17	0.41
7.7	13	0.53
24.4	5	1.38

Solution Volume: 70ml; H_2/CO = 1; Total Pressure = 1 MPa; Initial Gas Charge: 95 mmoles total, 15 mmoles C_2H_4, 0.13 mmoles C_3H_4, balance CO and H_2; Rh = 27.7 ppm, $[PPh_3]$ = 3.1%

Example 5

Gas solubilities were measured either by gas volumetric method using the same autoclave as in Example 1 or by ^1H NMR. In the autoclave experiments the solvent was thoroughly degassed in the autoclave before the gas was charged without stirring. After a short temperature equilibration the pressure and temperature in the autoclave was recorded and then the solvent was stirred until no further pressure drop could be observed. From the known gas volume and pressure drop the amount of dissolved gas was calculated. In the ^1H NMR experiments either the solvent (propanal) or hexamethylbenzene served as an internal standard. The values obtained are listed in Table 6.

Table 6. Experimentally Determined Solubilities for Hydrogen, Carbon Monoxide, Methane, Ethylene, and Acetylene at 0.1 MPa Partial Pressure

Solute	Solvent	Temperature (°C)	$X_i \times 10^4$	C_i (mmol/l)	Method
Hydrogen	Tetraglyme*	20	5.1	2.2	autoclave
		100	7.3	3.0	autoclave
	d^8-Toluene	22	3.5	—	NMR
Carbon monoxide	Tetraglyme*	20	11.3	4.9	autoclave
		100	34.6	14.2	autoclave
Methane	Tetraglyme*	20	30.0	13.7	autoclave
		100	63.0	26.3	autoclave
	Propanal	22	23.6	32.7	NMR
Ethylene	Tetraglyme*	20	134.0	60.0	autoclave
		100	76.0	32.6	autoclave
	Propanal	22	115.0	159.6	NMR
Acetylene	Tetraglyme*	20	1224.0	577.0	autoclave
		100	242.0	103.0	autoclave
	Toluene	20	246.7	220.6	autoclave
		100	178.0	147.7	autoclave
	Propanal	22	402.0	557.7	NMR

Legend: X_i = mol fraction of the gaseous component in the liquid phase, C_i = molarity of the gaseous component in the liquid phase

Note: * Tetraglyme containing 7.8 w.% PPh_3

The experimentally determined (see Table 6) and literature values (see Table 7) reflect high solubilities of ethylene and acetylene in oxygenates, especially in propanal. There is a large difference in solubility between ethylene and acetylene vs. all other major components of typical multicomponent syngas mixtures such as hydrogen, carbon monoxide, and methane. It can also be seen that the solubility difference increases with decreasing temperature.

Table 7. Gas Solubilities in Oxygenate Solvents

Solute	Solvent	Temperature (°C)	$X_i \times 10^4$	C_i (mmol/l)	Ref.*
Hydrogen	2-Methylbutanal	30	8.55	—	e
	2-Methylbutanal	100	11.45	—	e
	Formaldehyde diethyl acetal	30	5.37	5.07	g
	Propionaldehyde	100	5.95	—	k
	Methyl acetate	18	2.51	3.30	l
	Ethyl acetate	18	3.46	3.84	l
	1-Propyl acetate	18	4.15	3.99	l
	2-Propyl acetate	18	4.83	4.64	l
	1-Butyl acetate	18	4.29	3.64	l
	Methyl propanoate	18	3.77	4.19	l
	Methyl butanoate	18	4.67	4.49	l
	Ethylene glycol dimethyl	100	6.20	5.32	t
	ether	100	6.58	3.89	v
	2-Ethylhexanol-1	100	5.85	3.45	w
	2-Ethylhexanol-1	100	5.97	—	v
	2-Ethylhexanal-1				
Carbon	2-Methylbutanal	30	10.96	—	e
monoxide	2-Methylbutanal	100	13.93	—	e
Methane	Formaldehyde diethyl acetal	30	37.40	35.28	g
	Propionaldehyde	100	20.90	—	k
Ethylene	Formaldehyde diethyl acetal	30	185.00	174.53	g
Ethane	Formaldehyde diethyl acetal	30	214.00	201.89	g

Legend X_i = mol fraction of the gaseous component in the liquid phase, C_i = molarity of the gaseous component in the liquid phase

*Table 7 References

e) R A Aronovich, I I Vasil'eva, S M Loktev, V A Polyakov, E V Slivinskii, T N Tyvina Teor Eksp Khim 1991, 27(2), 241

g) L P Lizano, M C Lopez, F M Royo, J S Urieta J Solution Chem 1990, 19(7), 721

k) I I Vasil'eva, A A Naumova, A A Polyakov, T N Tyvina, V V Fokina Zh Prikl Khim 1987, 60(2), 408

l) E Brunner J Chem Thermodynamics 1980, 12, 993

v) N G Raginskaya, N G Tyurikova, N I Nechaiko Khim Prom-st 1979, 1, 21

w) E. Brunner Ber. Bunsenges. Phys. Chem. 79, 83(7), 715.

Example 6

The preparation and loading procedures of catalyst solutions were the same as in Example 1. The experimental method and the kinetic evaluation of experimental values were the same as in Example 3, except that 15 mmoles of ethylene was coinjected with 0.13 mmoles of one of the following dienes or acetylenes: 1,3-butadiene, allene, propyne, and acetylene. The catalyst charge was 18.8 μmoles of Rh (27.7 ppm), and 8.3 mmoles of PPh_3 (3.1 w.%) in each experiment.

Gas analysis of the gas reaction mixtures indicated a parallel conversion of ethylene with 1,3-butadiene, propyne, and acetylene. In the case of ethylene-allene mixtures, however, the conversion of ethylene could only start after essentially all the allene injected had been hydrogenated to propylene, as disclosed in Example 4. The final reaction mixtures contained essentially propanal, ethane, and the hydrogenated product of the coinjected highly unsaturated component. Thus 1,3-butadiene yielded butenes, and allene and propyne yielded propylene. At 95 to 98 % ethylene conversion the typical conversions of 1,3-butadiene, and propyne to the corresponding olefins were ca. 60 %. Since the hydrogenation product of acetylene is ethylene its intermediacy could not be detected in the hydroformylation of ethylene-acetylene mixtures. The observed reaction rates showed a different degree of inhibition on the oxo rate of ethylene by the highly unsaturated component. Thus, the observed turnover frequencies in ethylene hydroformylation with allene, 1,3-butadiene, propyne, and acetylene as coinjected reactants at 33% ethylene conversion were 3, 5.5, 7, and 9 mol propanal/mol Rh/sec, respectively.

Example 7

This example demonstrates the effect that small concentrations of acetylene have in stabilizing the rhodium catalyst against deactivation. The experiment involves two stages, an aging stage and a kinetic measurement stage. The preparation and loading procedures of catalyst solutions were the same as in Example 3, except that the autoclave and buffer bomb volumes are 500 and 325 ml, respectively.

For the aging stage of the experiment, 300 ml of catalyst solution was charged, which solution contained 1400 mmol tetraglyme, 30 mmol triphenylphosphine, and 0.3 mmol rhodium (96 ppm). These solutions were heated to 140°C at 1 MPa and contacted with one of three gas streams; (a) syngas (H_2/CO=1) alone, (b) syngas with 5 mol% ethylene, or (c) syngas with 0.51 mol% acetylene. In cases (b) and (c), the gas stream flow was controlled so that the substrate concentration in the effluent was maintained at about 0.5 mol percent. After aging times of 0 (initial solution), 80, 140, and 260 minutes, 30 ml samples of the catalyst solution were withdrawn and set aside.

For the kinetic measurement stage of the experiment, 200 ml of catalyst solution was charged, which solutions were prepared using the 30 ml samples of the aging stage and adding tetraglyme and triphenylphosphine to make a solution containing 860 mmol tetraglyme, 35 mmol triphenylphosphine, and 0.02 mmol rhodium (10 ppm). The experimental method for the kinetic evaluation was the same as in Example 3 (1 MPa, 120°C, H_2/CO=1) except that 20 mmoles of ethylene were coinjected with 3 mmoles of acetylene. The rate (mols oxo / second) was found to be first order in ethylene, and a rate constant for each kinetic experiment was calculated as mols oxo per mol ethylene, per wppm Rh, per second. For each aging experiment, rate constants were then normalized as a percent of initial (zero aging) catalyst activity.

A summary of the conditions and results of these catalyst deactivation experiments is shown in Table 8. It is well known that catalyst deactivation is rapid under conditions where substrate (olefin, alkyne) is absent, and this is confirmed in experiment (a) wherein the activity drops 90% in 260 min. at 140°C. Olefin hydroformylation is commonly run under conditions of low per-pass conversion in order to maintain substrate presence to mitigate this deactivation. Experiment (b) confirms that olefin presence reduces deactivation (now only 50% after 260 min), but also demonstrates that under the high conversion conditions that would be reflected in a ~0.5 mol% exit concentration, considerable deactivation occurs. In contrast, experiment (c) demonstrates that low (~0.5 mol%) concentrations of acetylene

dramatically reduce the deactivation (now only 5% after 260 min). Such a preservation of catalyst activity enables operation at higher per-pass conversion as well as higher temperatures.

Table 8. Catalyst Deactivation versus Substrate Presence

	(a) Syngas Alone	(b) Ethylene	(c) Acetylene
Aging Stage Conditions			
Gas Rate (nL/min)	1.0	4.5	4.2
Effluent Composition			
Ethylene, mol%	0.00	0.22 - 1.10	0.01
Acetylene, mol%	0.00	0.00	0.46
Propanal, mol%	0.00	3.40 - 4.20	0.02
Kinetic Rate Constant (% of initial) for samples withdrawn from Aging Stage			
Time of Sample			
0 min (initial solution)	100 %	100 %	100 %
80 min	42 %	84 %	90 %
140 min	22 %	69 %	95 %
260 min	10 %	49 %	95 %

Example 8

This example demonstrates the continuous hydroformylation of mixtures of olefin and cumulated diene, more specifically of ethylene and allene. Experiments were performed in a 500cc Autoclave Engineers Zipperclave stainless steel autoclave. The autoclave was equipped with a continuous gas feed system, with back pressure control, and with gaseous feed and product characterization via gas chromatography. Catalyst solution was prepared by mixing under nitrogen 210 g of tetraglyme, 15.8 g of triphenylphosphine, and 8.8 mg of rhodium (added as $Rh(CO)_2(acac)$, where acac is the acetylacetonato ligand). This corresponds to 39 wppm of Rh, and a P/Rh ratio of 700. Catalyst solution was transferred into the autoclave under nitrogen, the autoclave purged with nitrogen, and then gas flows commenced as indicated in Table 9. Pressure then built up to the 1000 kPa (abs) setting of

the back pressure control, after which the autoclave and contents were heated to 90°C reaction temperature Gas samples were taken after at least 20 hours of continuous reaction

Table 9 Continuous Hydroformylation of Ethylene and Allene

	(a)	(b)
Gas Flow Rates (ml/min)		
CO	250	250
H_2	1270	1270
CH_4	400	400
Ethylene	78	78
Allene	0.02	0.042
Observed Conversion		
Ethylene	56%	55%
Allene	>95%	89%

As shown in Table 9, ethylene and allene were simultaneously converted at these hydroformylation conditions In keeping with the high proportion of ethylene to allene, the products of these runs were predominantly propanal However, butanal was observed as reaction product

WHAT IS CLAIMED IS:

1. A process for the production of C_3 to C_6 aldehydes comprising hydroformylating a mixture containing:

(i) C_2 to C_5 olefins and mixtures thereof
and
(ii) C_2 to C_5 alkynes and mixtures thereof
and optionally
(iii) cumulated dienes

by reaction with CO and H_2 in the presence of a solution of a rhodium organophosphorus complex catalyst at a concentration of rhodium in solution of from 1 to 1000 ppm by weight.

2. A process for the production of C_3 to C_6 aldehydes comprising hydroformylating a mixture containing:

(i) C_2 to C_5 olefins and mixtures thereof
and
(ii) C_2 to C_5 alkynes and mixtures thereof
and optionally
(iii) cumulated dienes

by reaction with CO and H_2 in the presence of a solution of a rhodium organophosphorus complex catalyst at a concentration of rhodium in solution wherein the ratio of phosphorus to rhodium is greater than 30

3. A process for the production of C_3 to C_6 aldehydes comprising hydroformylating a mixture containing:

(i) C_2 to C_5 olefins and mixtures thereof
and
(ii) C_2 to C_5 alkynes and mixtures thereof
and optionally
(iii) cumulated dienes

by reaction with CO and H_2 in the presence of a solution of a rhodium organophosphorus complex catalyst wherein the catalyst solution has a P/Rh ratio greater than the value R_L wherein:

$$R_L = R_B + \frac{(30 - R_B) \bullet 10^{(pKa_{TPP} - pKa_L)}}{e^{(\Delta S_B / R)}}$$

wherein R_B is the P/Rh ratio sufficient for a catalytically active Rh complex, kPa_{TPP} is the pKa value for triphenylphosphine, pKa_L is the pKa value for the triorganophosphorus compound, R is the gas constant, and ΔS_B is 35(N-1) cal/mole °K, wherein N is the number of P-Rh attachments per ligand molecule, to product the corresponding C_3 to C_6 aldehydes.

4. A process according to claim 1 or claim 3 in which the ratio of phosphorus to rhodium is greater than 30.

5. A process according to any of the preceding claims in which the organophosphorus compound is triorganophosphorus.

6. A process according to any of the preceding claims in which the rhodium organophosphorus complex is oil soluble.

7. A process according to any of the preceding claims in which the rhodium is low valence.

8. A process according to any of the preceding claims in which the feed is multicomponent syngas.

9. A process according to any of the preceding claims in which the hydroformylation is performed at a temperature above 80°C.

10. A process according to any of the preceding claims in which on average the mixture is in contact with the catalyst for no longer than four hours.

11. A process according to any of the preceding claims in which a total concentration of coordinatively active P of at least about 0.01 mol/l is used.

12. A process according to any of the preceding claims in which a ratio of $[P]/p_{CO}$ of at least 0.1 mmol/l/kPa, where [P] is the total concentration of coordinatively active phosphorus in the solution, and P_{CO} is the partial pressure of CO is employed.

13. A process of any of the preceding claims wherein the olefin is essentially ethylene, and the alkyne is essentially acetylene.

14. A process according any of the preceding claims in which the mixture also contains dienes.

15. A process of any of the preceding claims wherein the partial pressure ratio of H_2/CO is from 1 to 100, the partial pressure ratio of CO/monounsaturates is from 0.5 to 100, and of H_2/monounsaturates is from 0.5 to 100

16. The process of any of the preceding claims wherein the oil soluble triorganophosphorous ligand is selected from the group consisting of oil soluble triarylphosphines, trialkylphosphines, alkyl-diaryl phosphines, aryl-dialkylphosphines, trialkylphosphites, and triarylphosphites having at least one phosphorus atom per molecule.

17. The process of any of the preceding claims wherein the reaction temperature is from 80°C to 180°C, the total pressure from about 0 05 to about 5 MPa the partial pressure of carbon monoxide up to 50 mol % of the total pressure, the mole % of H_2 is from 1 to 98 mole %, and mol % of ethylene and acetylene each alone and in combination is from 0 1 to 35 mol %

18. The process of any of the preceding claims in which the molar ratio of olefin to alkyne is at least 2

19. The process of any of the preceding claims wherein the contacting is carried out in at least two reactor stages

20. The process of claim 19 wherein the first stage is optimized at conditions for conversion of olefins in the presence of alkynes, and the second stage is optimized at hydrogenation conditions for conversion of alkynes to olefins

21. A process for recovering unreacted unsaturated hydrocarbons from an effluent stream of a process according to any of the preceding claims, comprising:

(a) absorbing the unreacted unsaturated hydrocarbons and the oxygenated hydrocarbons of the synthesis process effluent stream in a solvent wherein said solvent is an unsaturates-depleted stream of the oxygenated product of said synthesis process; and

(b) stripping the unsaturated hydrocarbons from the solvent to produce a first stream concentrated in unsaturates and a second stream of oxygenated product depleted in unsaturates, wherein said unsaturates-depleted stream is the absorption solvent and the synthesis process product

22. The process of claim 21 wherein the absorbing is carried out at a temperature between -100°C and +100°C.

23. A process for recovering unreacted unsaturated hydrocarbons from an effluent stream of a process according to any of claims 1 to 20, comprising

(a) partially condensing the effluent of the synthesis process to produce a liquid condensate enriched in the oxygenated product and a gaseous stream enriched in the low boiling gaseous components

(b) stripping the liquid condensate with an essentially unsaturates-free gas to produce an unsaturates-free oxygenated product and a gaseous stream enriched in unsaturates and low boiling gaseous components,

(c) combining the gaseous streams from step (a) and step (b) and cooling the combined stream,

(d) treating the combined stream from step (c) in an absorber having reflux of saturated hydrocarbon species at the top, to produce an overhead stream containing the low boiling gaseous components and substantially free of synthesis process product and unsaturated

hydrocarbon, and a bottoms steam of synthesis process product containing concentrated absorbed unsaturated hydrocarbon; and

(e) recycling said bottoms streams to the synthesis reactor.

24. The process of claim 23 wherein the bottoms stream of step (e) is pumped to high pressure and heat exchanged with the combined stream from step (c) to recover the cooling value.

25. The process of claim 23 or claim 24 wherein the treating of step (d) is carried out at a temperature between -100°C and +100°C.

26. A process for the preparation of a feed stream useful in the process of any of claims 1 to 25 comprising preferentially removing a variable amount of alkynes and multiunsaturates from a gas stream containing at least hydrogen, olefins, alkynes, and multiunsaturates comprising contacting the gas stream with a metal complex-containing stream at a rate sufficient to form adducts of the alkynes and multiunsaturates to be removed, and removing a stream containing the alkyne and multiunsaturate adducts of the metal complex.

27. A process according to claim 26 in which the metal complex stream is a liquid or a slurry.

28. The process of claim 26 or claim 27 wherein the metal complex is an oil-soluble rhodium complex containing a triorganophosphorous ligand selected from the group consisting of triarylphosphines, tralkylphosphines, alkyl-diaryl phosphines, aryl-dialkylphosphines, trialkylphosphites and triarylphosphites containing at least one phosphorus atom per molecule.

29. The process of claims 26 to 28 wherein the multiunsaturates are selected from the group consisting of C_3-C_5 conjugated and cumulated dienes, diynes, and enynes, the alkynes are selected from the group consisting of C_2-C_5 alkynes, and the olefins are selected from the group consisting of C_2-C_5 olefins.

30. The process of claim 29 wherein the gas stream is a multicomponent syngas mixture further comprising one or more of the gases selected from the group

consisting of CO, CO_2, C_1-C_5 alkanes, C_1-C_5 oxygenated hydrocarbons, nitrogen, water vapor, helium, and argon.

31. The process of any of claims 26 to 30 further comprising a separate regeneration step wherein the removed alkyne and multiunsaturate adducts of the metal complex are contacted with a hydrogen-rich, CO-depleted gas to form hydrogenated alkynes and multiunsaturates and a stream of regenerated, multiunsaturates-free metal complex.

32. The process of claim 31 wherein the regeneration step contacting is carried out at a H_2/CO partial pressure ratio of at least about 10, a total pressure of from about 0.1 to 50 MPa and a temperature of from about 50 to about 180°C.

33. The process of any of claims 26 to 32 wherein the metal complex containing stream is introduced at a rate sufficient to form adducts of the multiunsaturates without forming adducts of the alkynes.

34. A process comprising hydrogenating the aldehyde produced according to any of the preceding claims to form the corresponding alcohol.

35. A process comprising oxidizing the aldehyde produced according to any of the preceding claims to form the corresponding acid.

36 A process comprising aldolizing the aldehyde produced according to any of the preceding claims to form the corresponding aldol dimer.

37 A process according to claim 36 further comprising hydrogenating the aldol dimer to form a saturated aldehyde or saturated alcohol.

38. The process according to claim 36 further comprising oxidizing the aldol dimer to form the corresponding unsaturated acid.

39. A process comprising oxidizing the saturated aldehyde produced according to claim 37 to form the corresponding saturated acid.

40. A process comprising aldol condensing the aldehyde produced according to any of the preceding claims with formaldehyde to form multi-methylol alkanes.

41. The process of claim 40 wherein the aldehyde is propanal and the multi-methylol alkane is trimethylol ethane.

42. A process comprising further aldol condensing the aldol dimer of claim 36 with formaldehyde to form the corresponding multi-methylol alkane.

43. A process comprising further aldol condensing the saturated aldehyde of claim 37 with formaldehyde to form the corresponding multi-methylol alkane.

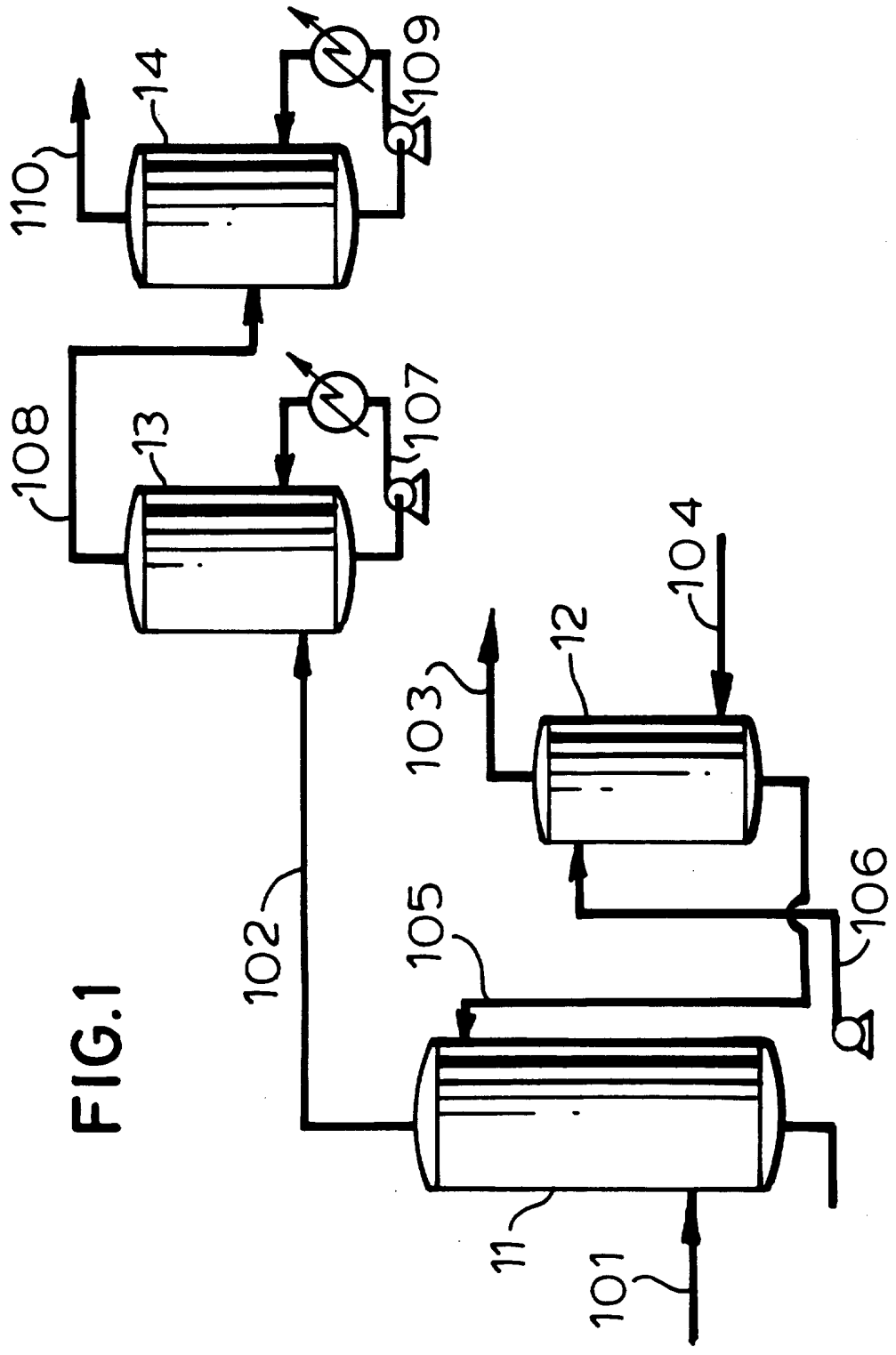


FIG.1

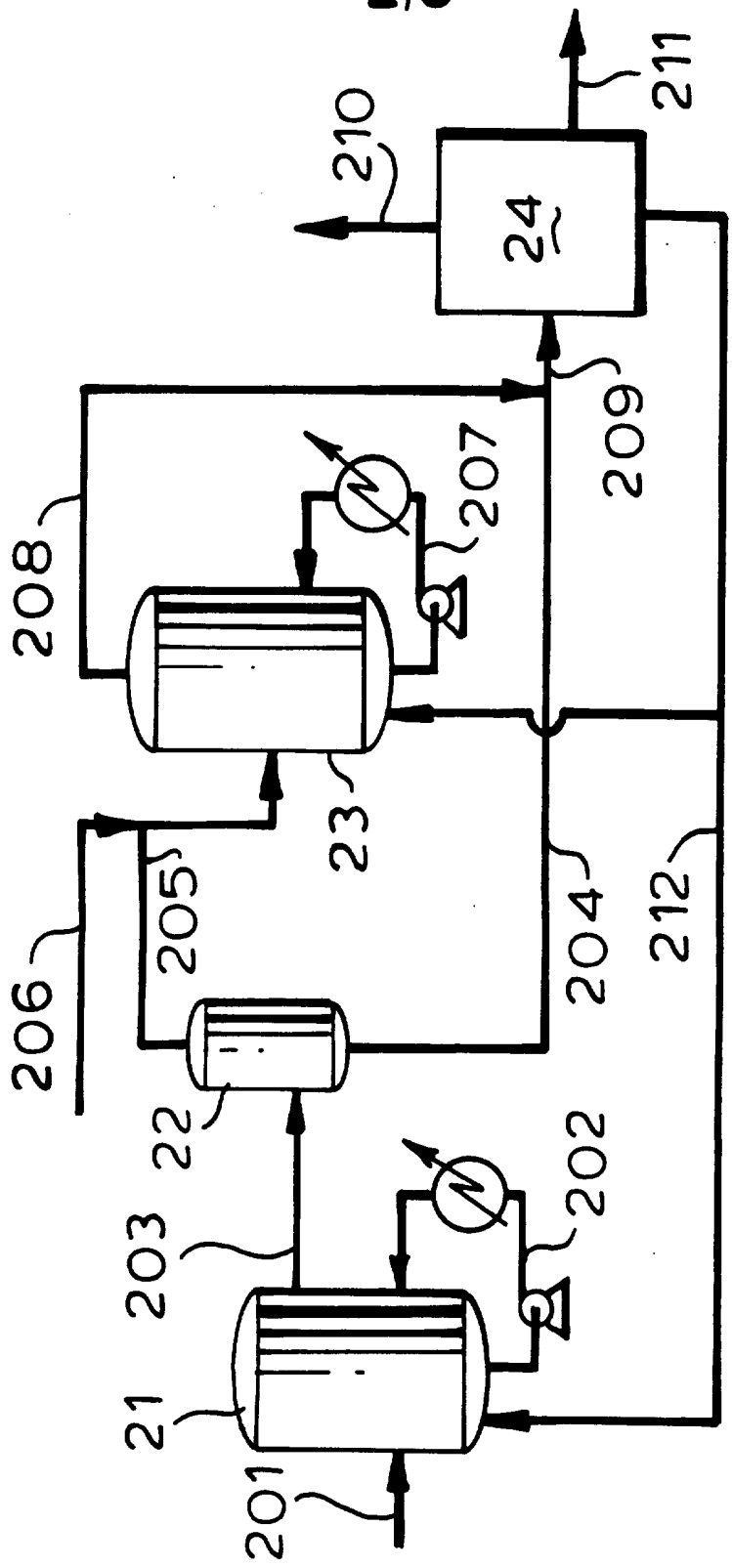


FIG. 2

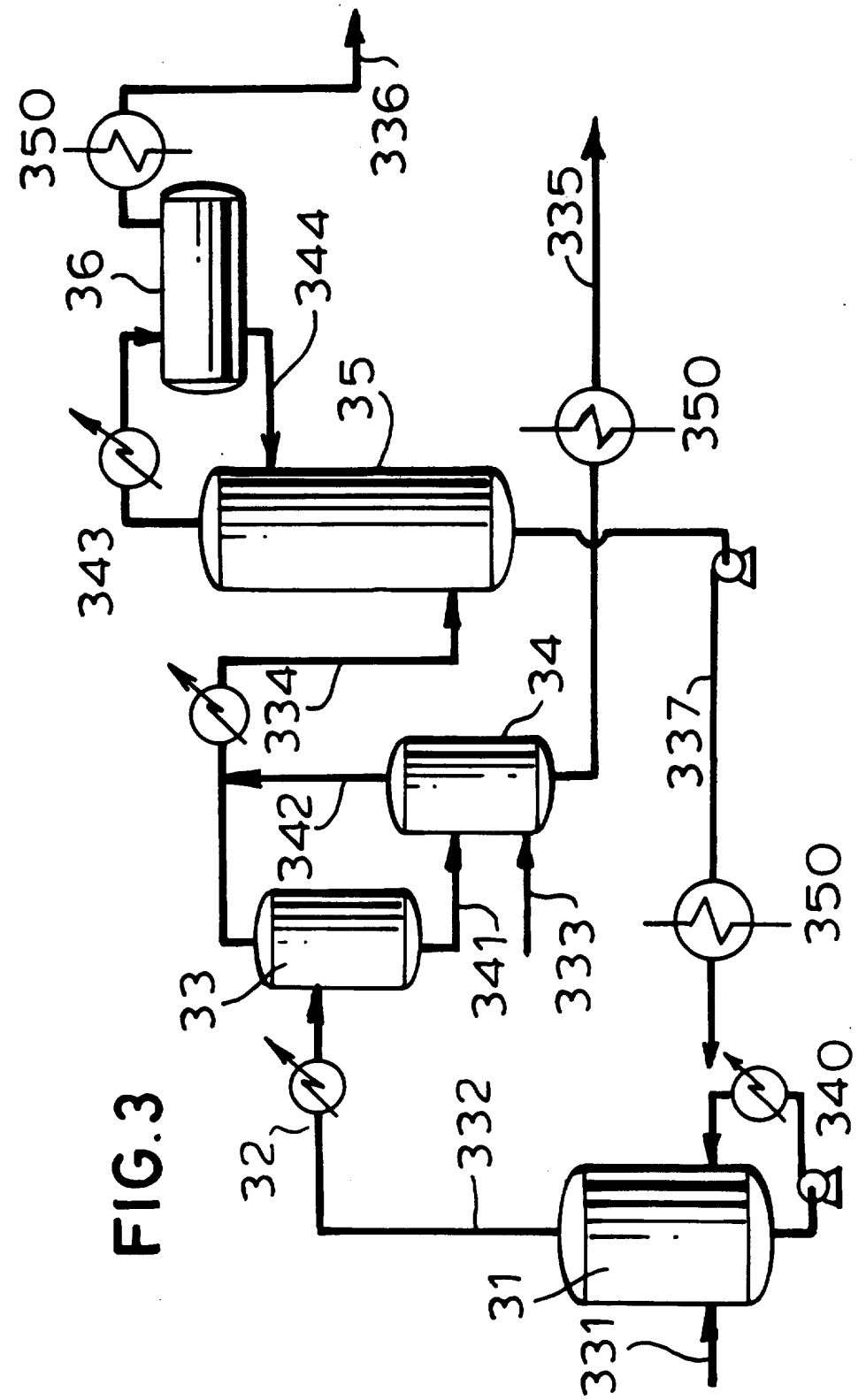

350
336
335
36
344
35
350
343
334
34
337
342
350
341
333
33
340
32
332
31
331

FIG.3

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/EP 96/00268

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C45/50

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)
IPC 6 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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 002, no. 041 (C-007), 17 March 1978 & JP,A,52 144608 (NISSAN CHEM IND LTD), 2 December 1977, see abstract ---	1
A	FR,A,1 042 618 (IMPERIAL CHEMICAL INDUSTRIES) 3 November 1953 see the whole document ---	1
A	EP,A,0 225 143 (BRITISH PETROLEUM CO PLC) 10 June 1987 cited in the application see the whole document ---	1
A	US,A,3 445 505 (WAKAMATSU HACHIRO ET AL) 20 May 1969 see the whole document ---	1

-/--

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

[X] Patent family members are listed in 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 document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
2 May 1996	10.05.96

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, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Bonnevalle, E

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/EP 96/00268

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ERDOEL KOHLE, ERDGAS, PETROCHEM. (EKEPAB);76; VOL.29 (4); PP.149-53, RHEINISCH-WESTFAEL. TECH. HOCHSCH.;AACHEN; GER., XP002001652 FELL B ET AL: "Hydroformylation of alkynes and allenes" see the whole document -----	1

1

INTERNATIONAL SEARCH REPORT

Intern: al Application No
PCT/EP 96/00268

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-1041618	26-10-53	NONE	
EP-A-0225143	10-06-87	NONE	
US-A-3445505	20-05-69	CH-A- 422746	
		CH-A- 443252	
		DE-B- 1285994	
		DE-A- 1543983	05-02-70
		FR-E- 90165	12-01-68
		FR-A- 1414264	07-01-66
		GB-A- 1080903	
		GB-A- 1144431	
		NL-A- 6413065	12-05-65
		NL-A- 6601896	16-08-66