

Letter

## *n*-Valeric acid: Expansion of the two phase hydroformylation to butenes

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Received 21 December 1995; revised 29 June 1996; accepted 2 July 1996

### Abstract

*n*-valeric acid (*n*-pentanoic acid) is the basis of new ester-type lubricants for CFC-substitutes in refrigeration systems which are made from the carboxylic acid with trimethylolpropane, pentaerythritol or dipentaerythritol. Together with UCC, Hoechst is one of the largest producers of *n*-valeric acid for this field of application. Valeric acid is prepared from butene cuts through hydroformylation to valeraldehyde with subsequent oxidation. The RCH-RP process of low-pressure hydroformylation [1] used at the Ruhrchemie side of Hoechst, involving an aqueous rhodium–TPPTS catalyst system (TPPTS = triphenylphosphane trisulfonate, sodium salt), has been used since 1984 to produce roughly 300,000 ton of *n*-butyraldehyde from propylene per year. A further development of this successful technology has been achieved using the available feedstock base of isomeric butenes (raffinate II) for the preparation of *n*-C<sub>5</sub> products (*n*-valeraldehyde, *n*/*iso*-amyl alcohol and *n*-valeric acid) [2]. The process developed permits high selectivity of the *n*/*iso* ratio to the desired *n*-aldehyde and it is environmentally benign as waste water contamination has been substantially reduced. In December 1995 production of *n*-valeraldehyde was started up in a new plant. Oxidation to produce the acid using the Hoechst/Ruhrchemie process is carried out with proven technology.

**Keywords:** Butene hydroformylation; Lubricants; Valeric acid

Aliphatic carboxylic acids are obtained in commercial processes by the hydroformylation of olefins with synthesis gas to produce the aldehyde and by subsequent oxidation to carboxylic acid. Apart from the original cobalt-based HP processes (HP = high pressure), rhodium-based LP processes (LP = low pressure) have gained increasing importance during the last ten years. LP hydroformylation with

rhodium results in much better selectivity to linear aldehydes and a high product yield.

The two-phase hydroformylation is a special development of homogeneous catalysis where a water-soluble catalyst complex (HRh(CO)[P(*m*-sulfophenyl-Na)<sub>3</sub>]<sub>3</sub>) reacts in the presence of synthesis gas with olefins to the corresponding aldehydes. Owing to their limited solubility the aldehydes formed can simply be separated from the aqueous catalyst phase and worked up. Basically, the oxo unit only consists a stirrer tank reactor and a decanter.

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The process developed for this purpose is based on the LP-Rh hydroformylation of propylene to *n*-butanal with a water-soluble Rh–TPPTS two-phase catalyst. The process has been successfully employed for 10 years to produce 300,000 ton of *n*-butyraldehyde per year. Removing the bottleneck of this process has now led to a total annual capacity of approximately 400,000 ton of C<sub>4</sub> products. It is therefore a logical step to expand this successful process to higher olefins.

Generally, there are strong restrictions in the application of the two phase catalyst process to higher olefins, due to the low solubility of these olefins in the aqueous catalyst solution. A lot of suggestions have been made to overcome this: a partial exchange of the sodium cations by detergent ammonium cations [3], the use of ultrasonic waves [4], the use of phasetransmitters like  $\beta$ -cyclodextrin [5], the extraction of partial watersoluble phosphines [6] and the use of the thermal reversible solvation (TSR) [7]. Fortunately, we found in our investigations that in case of butenes the use of additional aid and equipment is not required.

Raffinate II, an isomer cut from oil fractionation or from naphtha steam crackers, is a reasonably priced raw material for producing C<sub>4</sub> secondary products. A cut rich in 1-butene, which also contains butane in addition to 1-butene and 2-butene, is used for the hydroformylation to valeraldehyde.

The Rh–TPPTS catalyst system permits selective reaction of 1-butene to *n/iso* valeraldehyde. Product selectivities of over 95% of *n*-

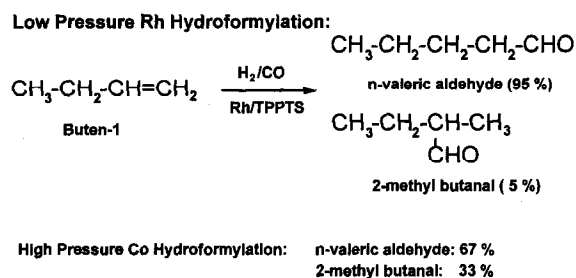


Fig. 1. Hydroformylation of raffinate II.

Table 1

Oxo raw products of *n/iso*-valeraldehyde – selectivity comparison between Co and Rh

	HP-Co process	LP-Rh process
<i>n</i> -valeraldehyde	55.7	92.5
<i>i</i> -valeraldehyde	26.8	5.0
<i>n</i> -pentylformate	2.7	trace amounts
<i>i</i> -pentylformate	1.5	trace amounts
<i>n</i> -pentanol	4.1	0.9
2-methylbutanol	2.5	0.1
Heavy ends	6.7	< 1.5
<i>n/iso</i> ratio	67/33	95/5

valeraldehyde and the corresponding amount of 2-methylbutanal are obtained (Fig. 1) due to the high regioselectivity of the catalyst.

A comparison with the previous HP-Co process mainly for the preparation of amyl alcohol shows a significant increase in selectivity (*n/iso*-ratio 67/33 in the Co process as against 95/5 in the Rh process). Moreover, the use of the LP-Rh process greatly improves the waste water situation and results in a waste water-free process and efficient raw material use in comparison to the HP-Co route.

A clear impression of the advantages of the LP-Rh process can be gained by comparing the oxo raw products obtained from this process and those from the HP-Co process (Table 1). A considerable improvement can be seen both in the spectrum of by-products and the high boiler content.

In the Co process formates are obtained through additional carbonylation of the aldehydes already obtained. The hydrogenating activity of Rh catalyst systems, i.e. the formation of amyl alcohol, is much lower (Table 1).

Furthermore, the formation of high-boiling products which result from the secondary reaction of the aldehydes formed (acetalization, condensation, trimerization) is reduced mainly owing to lower reaction temperatures. There is a considerable improvement in selectivity.

The process taking place in the LP-Rh hydroformylation stage is shown using a simplified reaction diagram (Fig. 2). Raffinate II is fed into an intimately mixed reactor and reacted with the

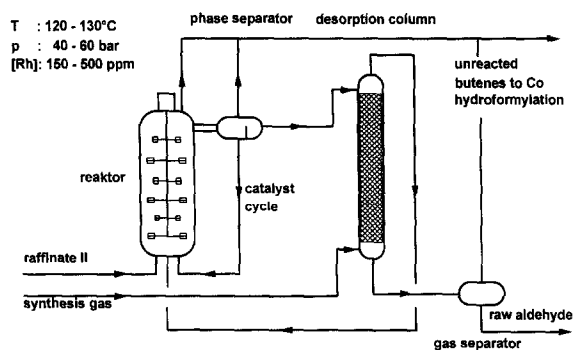


Fig. 2. LP-Rh hydroformylation (plant diagram).

aqueous catalyst phase in the presence of synthesis gas. In a downstream phase separator the aldehyde phase is separated from the aqueous catalyst which is fed through a catalyst circulation system back into the reactor. The content of inerts, which includes 2-butene in addition to butane, is controlled by a reactor and phase separator waste gas stream. The organic phase containing dissolved amounts of unreacted butenes is fed into a desorption column which is operated in counter-current with pure synthesis gas. At this point butene is fed back into the reactor by means of a cycle gas stream. The raw aldehyde forming at the bottom of the column is pressure-released and passed on for further work-up.

The desorption column plays a key role in this part of the reaction as the inerts content in the cycle gas stream has a major impact on the reaction. In a second HP-Co process stage the unreacted butenes are reacted by hydroformylation and hydrogenation to isomeric amyl alcohols. Inert constituents (mainly butane) are fed to the power station for power generation.

The raw aldehyde obtained in the hydroformylation stage is first separated by distillation from the isovaleraldehyde contained in it. Final oxidation takes place with pure oxygen according to the Hoechst/Ruhrchemie process in an existing plant. The technology of the

catalyst-free co-current oxidation stage has been successfully used to produce aliphatic carboxylic acids for thirty years now. The process is also used, among other things, to produce C<sub>7</sub>, C<sub>9</sub> and other higher molecular acids. It can be operated at normal pressure and at moderate temperatures with very good selectivities [8].

Many years of production experience with the LP-hydroformylation of propylene and HP-Co technology and the knowledge thus gained have been used to develop a new commercial process for the production of *n*-valeric acid.

*n*-valeric acid, in the form of the ester with trimethylolpropane or pentaerythritol, is the basis of new ester-type lubricants which are used with CFC-substitutes in refrigeration systems. The market for this product group will expand in the medium long term for ester-type lubricant applications.

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