

CHAPTER-3

SYNTHETIC ROUTES OF 2-ETHYL HEXANOL PRODUCTION :

The industrially significant synthetic pathways are:

Acetaldehyde route	(A) → (F) → (N)
Oxo Route	(B) → (C) → (G) → (N)
Aldox Process	(B) → (M)
Shell Variant	(B) → (L)

The acetaldehyde route starts from ethylene and operates at near atmosphere pressure. Ethylene is first oxidized to acetaldehyde, which is then converted to crotonaldehyde via aldol reaction & hydrogenated to n-butyraldehyde. Route (a) → (f)

The most important synthetic route accounting for over 95% of 2-EH production is based on propylene which after initial hydroformylation is converted into an Oxo crude product. (Routes (b) → (c) → (g)). The crude Oxo product is a mixture of valuable products of propylene hydroformylation (n - and iso – butyraldehyde) along with the byproducts (n – and iso – butanol) and the heavy ends. The individual components of the mixture can be obtained after distillation.

n – Butyraldehyde is converted into butyraldol via an alkali catalyzed reaction and then crotonized to 2-Ethylhexanol (Route (n)). Thereafter, 2-Ethylhexenal is either partially hydrogenated to 2-ethylhexanal or undergoes total hydrogenation to 2-EH.

The n-component mixture of n- and iso – butyraldehyde can be selectively converted into 2-Ethylhexenal and then further processed to 2-EH (Route (H)). However, due to the presence of iso-butyraldehyde and the unavoidable formation of isomeric n/iso and iso/iso aldols (or C₈ diols), the quality of the resulting 2-EH is inferior to that of the product obtained directly from n-butyraldehyde.

Aldox process is a case in which co-catalysts are added to the actual Oxo catalyst enabling aldolization to occur in the same phase. Consequently, after hydrogenation, a mixture results consisting of 2-EH, isomeric C₈ alcohols & isobutanol (Route (m)).

In the shell process a complex (ligand-modified hydroformylation catalyst) $\text{HCo}(\text{CO})_3(\text{PR}_3)_3$ – is employed. This permits operation at lower pressure and higher selectivity i.e. at a higher n/i ratio. However, the reaction velocity is lower & part of the propylene is converted to propane.

Basically similar reservations pertaining to the quality of the resulting 2-EH also apply to the processing of the heavy ends of the Oxo synthesis (Route (j)) which also yields 2-EH after additional hydrogenation. However, one drawback is that in molar terms only 2/3 of the butanol feedstock is converted into 2-EH, the remaining third resulting as sodium butanoate.

The reaction of 2-EH with 2-Ethylhexenal in which the very reactive unsaturated aldehyde can be removed from the reaction mixture via reduction to the saturated aldehyde (Route (o)) belongs to the more specialized but not industrially operated methods: Removal of

2-Ethylhexenal prevents its conversion into higher boiling compounds.

**COMPARISON OF COAL BASED ROUTE & PETROCHEMICAL
ROUTE.**

The figure clearly indicates that the transition from the coal based route to the petrochemical route led to a reduction in the number of processing steps.

Therefore over 95% of the Current 2-EH production is based on propylene.

Process description

Oxo Reactor (Hydroformylation):

The first step of the process is Hydroformylation (Oxo reaction) from which the main product is n-butyraldehyde. The reactor operates at 130⁰C and 350 bars. The reactor residence time is 1-2 hours.

The feeds to the reactor are synthesis gas (CO/H₂ mixture) and propylene in the molar ratio 2:1. The catalyst used is Cobalt Carbonyl in the solution (0.1-1.0 wt% Cobalt concentration).

The synthesis gas may contain several percent methane, which acts as an inert in the reactor. Traces of water introduced with the synthesis gas are not harmful. Impurities such as hydrogen sulfide and triethylamine should be carefully excluded, however to prevent reaction with the active cobalt complex to form catalytically inactive complexes.

Oxygen should be excluded from the system, during the start up phase when the active catalyst concentration is being established. Oxygen has been shown to inhibit cobalt hydrocarbonyl formation, but once the system is operating, concentration up to 2% can be tolerated. CO₂ acts in the same manner as oxygen, with concentration up to 4% permissible.

Polymer grade (99+%) pure propylene may be fed. Propylene feed should be vaporized & fed into the reactor as a gas. Designing for propylene conversions of greater than 95% per pass will minimize propylene losses in the blowdown vent stream.

The main reaction products are n- and iso butyraldehyde in the ratio of 4:1, the former being the required product for subsequent conversion to 2-Ethylhexanol. Within the reactor, however 6% of n-butyraldehyde product is reduced to n-butanol, 4% of iso-butyraldehyde product is reduced to iso-butanol & other reactions occur to a small extent yielding molecular weight compounds (heavy ends) to the extent of 1% by weight of the butyraldehyde/ butanol mixture at the reactor exit.

Separator:

In the separator, which follows the Oxo-reactor, the catalyst solution is separated from the oxo-raw product & recycled to the Oxo reactor.

Stripper:

In the stripper, the unconverted propylene is removed from the Oxo-product using fresh synthesis gas. This synthesis gas is recycled to the Oxo reactor.

Distillation Column (1): Alcohol/Aldehyde Separator

The Oxo-product from the stripper passes to a distillation column, which gives a top product of mixed butyraldehyde & the bottom product alcohols.

Distillation Column (2): n- and iso Butyraldehyde Separator

The butyraldehydes are passed into a 2nd distillation column which separates the two butyraldehydes into an iso-butyraldehyde (top) stream containing 1.3% moles n-butyraldehyde & an n-butyraldehyde (bottom) stream containing 1.2% mole is butyraldehyde.

Aldolization:

The n-butyraldehyde stream passes on into an Aldolization reactor. In the Aldolization reactor, n-butyraldehyde reacts very quickly to give 2-Ethylhexanal. 2% w/w aqueous NaOH is employed as the standard industrial catalyst. The conversion efficiency is 90%. The temperature is 80-130⁰C & pressure 3-10 atmospheres.

Local overheating in the reaction mixture must be avoided since this may cause secondary reactions & thus decrease yields. Thorough mixing of the 2-phases in the system is necessary.

The Aldolization reactor may be a mixing pump, a packed column or a stirring vessel.

Separator:

The product from the Aldolization reactor passes on to a separator where 2-Ethylhexanol is separated and then sent to a hydrogenation unit.

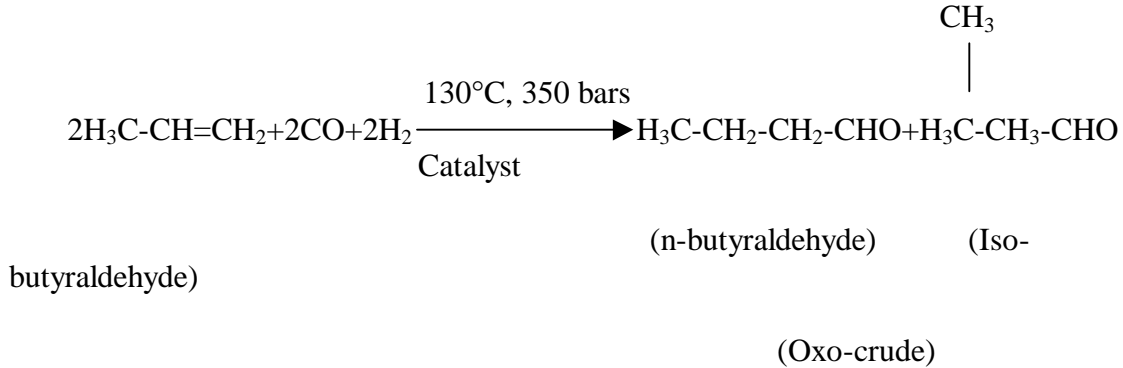
Hydrogenerator:

The 2-Ethylhexanal is reduced to 2-Ethylhexanol by hydrogen in the presence of a Raney Nickel Catalyst with a 99% conversion rate. The selectivity attained is greater than 99%.

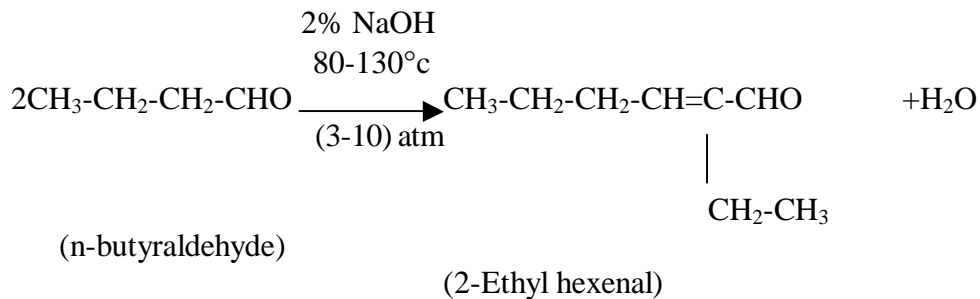
In the subsequent stages 99.8% of 2-Ethyl hexanol is recovered at a purity of 99% by weight.

CHEMICAL REACTIONS

(1) Reaction of Propylene with synthesis gas :



(2) The Aldolization and subsequent Conversion to 2-Ethyl Hexenal :



(3) The Hydrogenation to 2-Ethyl Hexanol :

