

84-068990/11 UNION CARBIDE CORP 16.03.82-US-358703 (+US-971667) (28.02.84) C07c-27/06 Alcohol and glycol prodn. from synthesis gas - using homogeneous ruthenium carbonyl catalyst in polar solvent	E17 UNIC 21.12.78 *US 4434-247-A	E(10-E4B, 10-E4E) N(4-D1, 5-B)  109
C84-029607	Full Priorities: 21.12.78(2), 15.11.79, 26.9.80, 16.6.82-US-971667, 9 71816, 091242, 190988, 358705.  Continuous prodn. of MeOH, EtOH and ethylene glycol (EG) comprises introducing H <sub>2</sub> and CO into a liq. phase maintained at 50-400 (pref. 100-350)°C and 500-15,000 (pref 500-12,500) psia to form MeOH, EtOH, EG and EG reaction prods., and repeatedly removing the liq. phase before the EG concn. exceeds 20 wt. % of the liq. phase and the EG reaction prod. concn. exceeds 50 wt. % of the total concn. of EG and its reaction prods.  The liq. phase contains a solubilised ruthenium carbonyl complex and a solvent having dielectric constant $\geq 2$ , as measured at 25°C or its m. pt., whichever is the higher.  <u>ADVANTAGES</u> The process gives significant EG yields at lower	pressures than in prior art processes.  <u>DETAILS</u> The solvent is pref. a liq. which is polar or complexes ions. Specified solvents are water, sulphones, lactams, ethers (esp. crown ethers, alkylene glycol alkyl ethers or polyalkylene glycol dialkyl ethers, e. g. tetraglyme), lactones (esp. butyrolactone) and carboxylic acids (esp. acetic acid). The solvent may act as a promoter, or a Lewis base promoter may be added, pref. in an amt. of 0.001-100 mmoles per g-atom of Ru. Specified promoters are alkali metal halides (esp. iodides) and acetates. The liq. phase may be removed intermittently or esp. continuously, pref. before the EG concn. exceeds 15% and the EG reaction prod. concn. exceeds 30 wt. % of EG+ prods.  <u>EXAMPLE</u> An autoclave was charged with 2.34 mmoles Ru <sub>3</sub> (CO) <sub>12</sub> , 14.9 mmoles LiI and 40 ml sulpholane, pressurised with 3000 psig H <sub>2</sub> + CO (1 : 1) and heated at 230°C and 5000 psig for 2 hr. Yields were 0.1g EG, 4.25g MeOH and 0.25g EtOH.  US4434247-A  (19pp367DAHDwgNo0/1)

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28979 E/15 E17 UNIC 26.09.80  
 UNION CARBIDE CORP \*EP--48-980  
 26.09.80-US-190988 (07.04.82) C07c-29/15 C07c-31/20 C07c-  
 67/36 C07c-69

Ethylene glycol, methanol and ethanol prodn. - from synthesis gas using ruthenium catalyst

E(10-E4B, 10-E4D, 10-E4E, 10-G2B, 10-G2E) N(5-B)

052

phase pref. also contains a promoter, pref. a Lewis base, an alkali metal halide (esp. iodide) or an alkali metal acetate. The promoter concn. can be 0.1-1,000,000 moles per g.-atom of Ru. To maximise EG prodn., the process is pref. operated continuously and the liq. phase removed from the reactor before the EG concn. exceeds 20 wt. % and before the concn. of EG reaction prods. (acetals, ethers, etc.) exceeds 50 wt. % of the total glycol prods.

#### EXAMPLE

An autoclave was charged with 2.34 mmole  $Ru_3(CO)_{12}$ , 14.9 mmole LiI and 40 ml. sulpholane, pressurised to 5000 psig with a 1 : 1 mixt. of  $H_2$  and CO, and rocked at 230°C for 2 hr. The prods. comprised 0.1g. EG, 4.25g. MeOH and 0.25g. EtOH. (79pp367).

(E)ISR: GB2058600 US4225530 EP--13008.

D/S: E(BE DE FR GB IT NL SE)

Prodn. of methanol, ethylene glycol (EG) and ethanol, or their carboxylate derivs., comprise contacting  $H_2$  and CO at 50-400 (pref. 100-350)°C and 500-15,000 (pref. 500-12,500) psia with a liq. phase comprising a solubilised ruthenium carbonyl complex in a solvent having dielectric constant  $\geq 2$  (as determined at 25°C or at its m.pt., which ever is higher).

#### ADVANTAGES

The process is operated at relatively low temps. and uses a less expensive catalyst than prior art processes.

#### DETAILS

The solvent can be (a) a polar solvent, pref. water or a sulphone, lactam or lactone (esp. butyrolactone), (b) a complexing solvent, pref. an ether, esp. a crown ether or a polyalkylene glycol dialkyl ether, or (c) a carboxylic acid (esp. acetic acid) which forms carboxylate prods. The liq.

EP--48980