88-198015/28 E17 H04 (H06) **ESSO 22.12.86**
EXXON RES & ENG CO *US 4754-092-A
30.12.85-US-814680 (+US-944656) *(28.06.88)* C07c-01
**Reducing methane prodn. in Fischer-Tropsch hydrocarbon synthesis - by adding olefin to gas feed contg. hydrogen and carbon monoxide at interior of catalyst bed**
**C88-088448**

E(10-12D) H(4-E5) N(2-A1, 2-B1, 2-E)

Process for reducing methane formation and increasing liq. ($C_5$+) yields in a Fischer-Tropsch hydrocarbon synthesis comprises adding an olefin to a gas feed comprising $H_2$ and CO and contacting with a catalyst at at least 100°C. Olefin addn. and contact occurs within the reactor bed in the area between the top 10% of bed depth and the bottom 10% of bed depth. The catalyst comprises Fe, Co or Ru on an inorganic refractory oxide support.

USE/ADVANTAGE

Useful in prodn. of chemical feedstocks and liq. fuels. Suppression of methane prodn. increases the value of the prod.. Addn. of the olefin to the interior of the catalyst bed decreases hydrogenation of the olefin to unreactive alkanes. The olefin may be obtained from the prod. stream.

MORE SPECIFICALLY

2-15C, esp. 2-10C alpha-olefins are prefd. Olefin : CO molar ratio is 1/100-5/1, and $H_2$ : CO molar ratio is 0.5-10.

Catalyst support is pref. $TiO_2$. Prefd. catalytic metal is Ru, at 0.01-50, esp. 0.5-5 wt.% of total catalyst.

Reactor is at 100-500 (150-300), esp. 210-270°C, and a pressure of 100-10,000 (300-5,000), esp. 500-3,000 kPa.

Feed gas ($H_2$ + CO) space velocity ($V_1$) is 10-10,000 (100-4,000), esp. 200-2,000 standard $cm^3$./hr. - ($cm^3$ catalyst), and olefin space velocity ($V_2$) is 0.1-20,000 (3-4,000) esp. 10-2,000 standard $cm^3$./hr.-($cm^3$. catalyst).

EXAMPLE

Ethylene was added at 6.2% to $H_2$/CO (2.1/1) feed and reacted over 1.2% Ru/$TiO_2$ at 200°C., 1,700 kPa. CO conversion was 35-45%.

Addn. of ethylene below the top 1/3 of the reactor gave 45.3% ethylene conversion, c.f. 97% for addn. at reactor top. Selectivity to ethane was 44% cf. 82%, to $C_3$+ was 56% cf. 18%, and to $CH_4$ was 3.9% cf. 4.3%.(6pp1762RKDwgNo0/0).

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