

Supplementary Information

1) The preparation method of typical catalysts

The heterogeneous Mn catalysts were prepared using the following procedure.

The MnTiO₃ catalyst: An aqueous dispersion of MnCO₃ (Wako Pure Chemical Industries, Ltd.), TiO₂ (anatase, Wako Pure Chemical Industries, Ltd.) and the alkylated cellulose (METOLOSE, Shin-Etsu Chemical Co., Ltd.) was prepared. The mixture was pelletized and then calcined at 1000°C for 5 hours in air after drying at 120°C. The BET specific surface area was 1 m²g⁻¹, determined by N₂ adsorption at 77 K.

The Mn-Al mixed oxide: Activated alumina beads of 150 mesh size (AC-12, Sumitomo Chemical Co., Ltd.) were impregnated with an aqueous solution of manganese (II) nitrate (Wako Pure Chemical Industries, Ltd.). The crude mixture was then dried at 120°C and calcined at 800°C for 5 hours in air. The Mn:Al atomic ratio in the catalyst was 1:14 and the BET specific surface area was 84 m²g⁻¹.

2) The reaction methods using the continuous-flow fixed bed reactor under subcritical conditions

The transesterification reaction of palm oil in the subcritical phase was carried out isothermally in a continuous down-flow tubular reactor (SUS316 tubular reactor with a Swagelok VCR joint, 1/2 inch x 10mm x 220mm). The reactor was loaded with catalyst particles and placed in an oven. A mixture of refined palm oil and methanol was independently introduced into the reactor through the preheating mixing coil with its own HPLC pump. The pressure in the reaction system was controlled by an automatic back pressure regulator (ER-3000, TESCOM/Emerson Corp.) at 5 MPa. Standard reaction conditions were used (15-mL catalyst, 200°C, 5 MPa, a flow ratio of palm oil/methanol = 1/1 by weight and the LHSV (ml-liquid/ml-cat·hr) is 1 hr⁻¹; which is the liquid hourly space velocity, calculated based on the liquid flow rate of a solution of mixed reactants at atmospheric temperature and pressure).

The chemical yields of the products were determined by gas chromatography analysis (GC-2010, Shimadzu Corp.; FID detector and DB-FFAP (for FAME) and DB-17ht (for glycerides) capillary columns, Agilent J&W; using anisole and 1,3-dimethoxybenzene as the internal standards, respectively) and the conversion of triglycerides was determined by UPLC analysis (Acquity UPLC, Waters Corp.; PDA detector). Analysis of di- and monoglycerides were carried out by GC after derivatization to silylethers. Conversion of triglyceride X_a , yield Y_e of FAME and yield Y_n of each glyceride -product, i.e. glycerin, monoglycerides and diglycerides were defined as:

$$X_a = (F_{a(\text{ini})} - F_a) / F_{a(\text{ini})} \times 100 (\%) \quad (1)$$

$$Y_e = F_e / [F_{a(\text{ini})} \times 3] \times 100 (\%) \quad (2)$$

$$Y_n = F_n / F_{a(\text{ini})} \times 100 (\%) \quad (3)$$

$F_{a(\text{ini})}$ and F_a represents molar flow rates of reactant palm oil at the reactor inlet and outlet, respectively, and F_e and F_n represents that of FAME and glycerides-products at the reactor outlet, respectively.

During the reaction, no degradation products of methanol, such as dimethylether, carbon monoxide and methane were detected. Methanol was only consumed as a reactant in the transesterification reaction.

Leaching of metal species was checked by an ICP-AES analysis (CIROS-120, SPECTRO Analytical Instruments GmbH) of the diluted homogeneous samples of the product two-phase solution with methyl isobutyl ketone solvent.

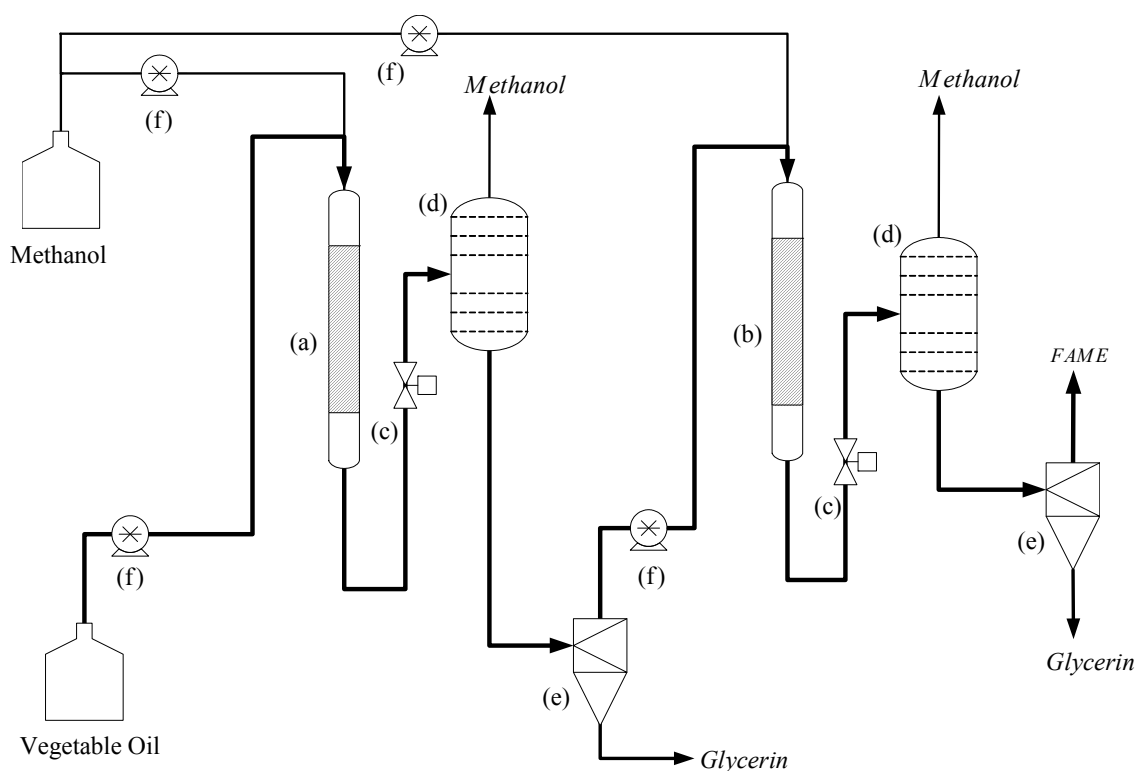
3) The model reaction of manganese diacetate with methanol to methylacetate

The manganese diacetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$; Wako Pure Chemical Industries, Ltd., 5 g / 0.02 mol) was dissolved in methanol (15 g / 0.30 mol), and refluxed at 70°C at atmospheric pressure for 8 hours. Some brown solid was precipitated and methylacetate was generated (10 mol% yield) by GC analysis of the liquid phase (GC-2010, Shimadzu Corp.; FID detector and DB-1 capillary column, Agilent J&W; using 2-ethoxyethanol as the internal standard).

4) The bench-scale two-stage reaction system comprised the consecutive two fixed-bed reactors with the flash evaporator and the settler

- (a) The first reactor; 8 cm ϕ x 220 cm, Austenitic stainless steel 316
- (b) The second reactor; 8 cm ϕ x 160 cm, Austenitic stainless steel 316
- (c) The back pressure regulator, MOTOYAMA ENG. WORKS, LTD.
- (d) The flash evaporator; 8 cm ϕ x 100 cm, Austenitic stainless steel 316
- (e) The settler; 6 cm (W) x 48 cm (L) x 10 cm (H), Austenitic stainless steel 316
- (f) The feed pump, diaphragm metering pump, NIKKISO CO., LTD.

The typical capacity for FAME production was 60 kg per day.



[Fig. 4]