# Hydroformylation of Methyl Oleate with a Recycled Rhodium Catalyst and Estimated Costs for a Batch Process[1]

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## ABSTRACT

Methyl oleate was hydroformylated to methyl formylstearate at 120 C and 850-900 psig with a 1:1 mol mixture of hydrogen and carbon monoxide. In the presence of triphenylphosphite, an activated rhodium-on-alumina catalyst produced an essentially quantitative conversion in about 40 min. Filtration followed by distillation yielded methyl formylstearate. The solubilized rhodium catalyst was concentrated in the distillation residue. The residue was resupported on the spent support in a gas-fired rotary kiln. The process was repeated 9 times without significant loss of catalyst activity. Assuming the catalyst can be recycled repeatedly to the process without affecting the efficiency of operation, a preliminary estimate based on a hypothetical plant producing 2 million lb of methyl formylstearate annually places the processing costs, not including cost for methyl oleate, at about 13.7 cents per pound.

## INTRODUCTION

Among the reactions of carbon monoxide with unsaturated fatty derivatives (1), hydroformylation has received considerable attention (2,3), especially at the Northern Regional Research Laboratory, Peoria, Ill. (4-6). The conventional method involving a cobalt-carbonyl catalyst presents several disadvantages for the hydroformylation of fatty derivatives. Cobalt carbonyl-catalyzed hydroformylations not only require high temperatures and pressures but produce mixtures of aldehydes and alcohols. Alcohols are undesirable if the production of carboxylic acids is the ultimate goal. The high temperatures also cause a large number of positional isomers to form.

By comparison, a supported rhodium catalyst in combination with triphenylphosphine gives an excellent conversion of methyl oleate (MO) to methyl formylstearate (MFS) at 110 C and less than 1000 psi as reported by Frankel (5). Furthermore, no alcohols are formed, and under certain conditions the reaction is selective and yields 9(10)-MFS almost exclusively.

The primary disadvantage of the rhodium-triphenylphosphine system has been catalyst cost since no method has been devised for catalyst recovery and regenration. Roughly 50-80% of the supported rhodium is solubilized in the crude MFS. This soluble rhodium catalyst (SRC) is nonvolatile and can be concentrated by distillation of MFS; however, the distillation residues are only slightly active and cannot reasonably be reused in that form. The complexing agent, triphenylphosphine, is not recovered but is either decomposed or distilled with the MFS. This paper reports a practical method for regeneration of SRC from distillation residues. It also reports a process, with attendant cost analysis, for the production of MFS from MO using this activated rhodium catalyst (ARC) in combination with triphenylphosphite (TPP) (35 cents/lb) rather than triphenylphosphine ($10/lb).

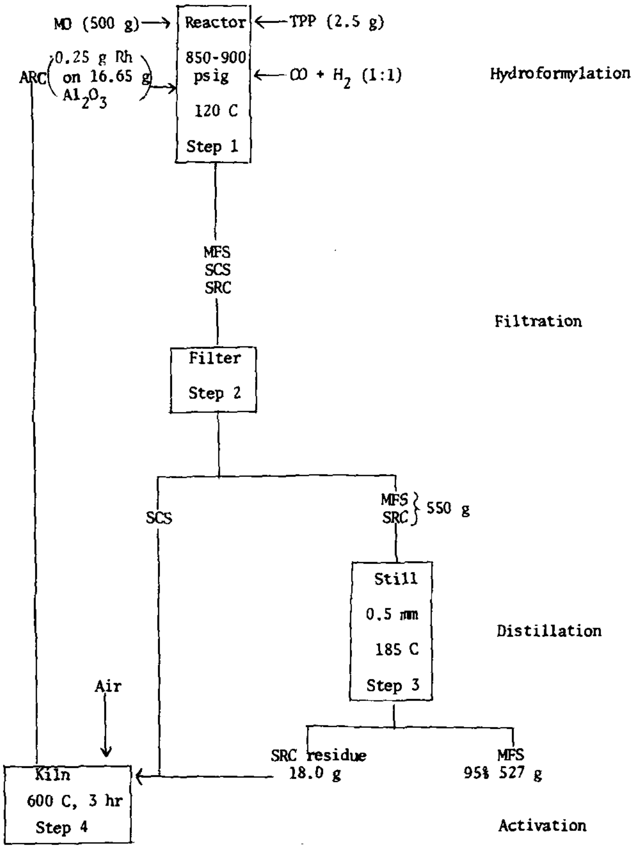

FIG. 1. Semi-quantitative flow diagram of a batch process for preparation of methyl formylstearate (MFS). Methyl oleate (MO), triphenylphosphite (TPP), activated rhodium catalyst (ARC), spent catalyst support (SCS), and soluble rhosium catalyst (SRC).

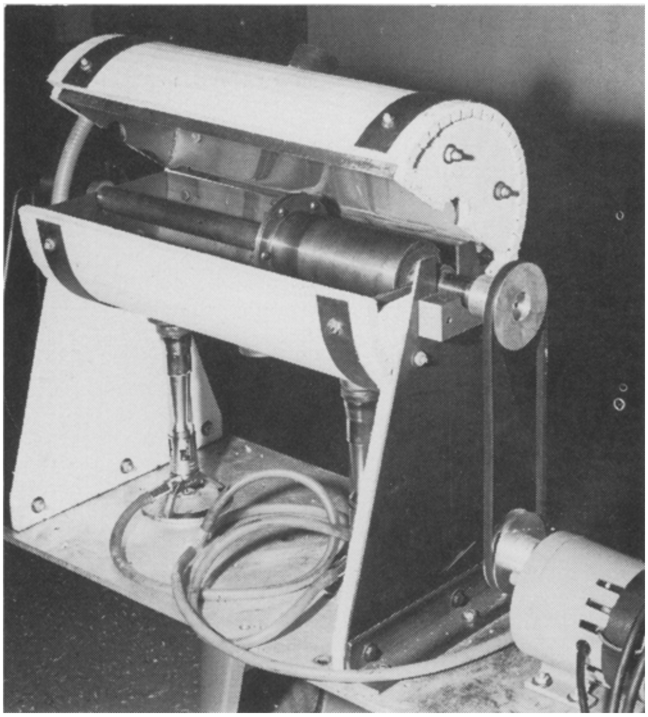

FIG. 2. Rotary kiln for the deposition and reactivation of soluble rhodium contained in distillation residues.

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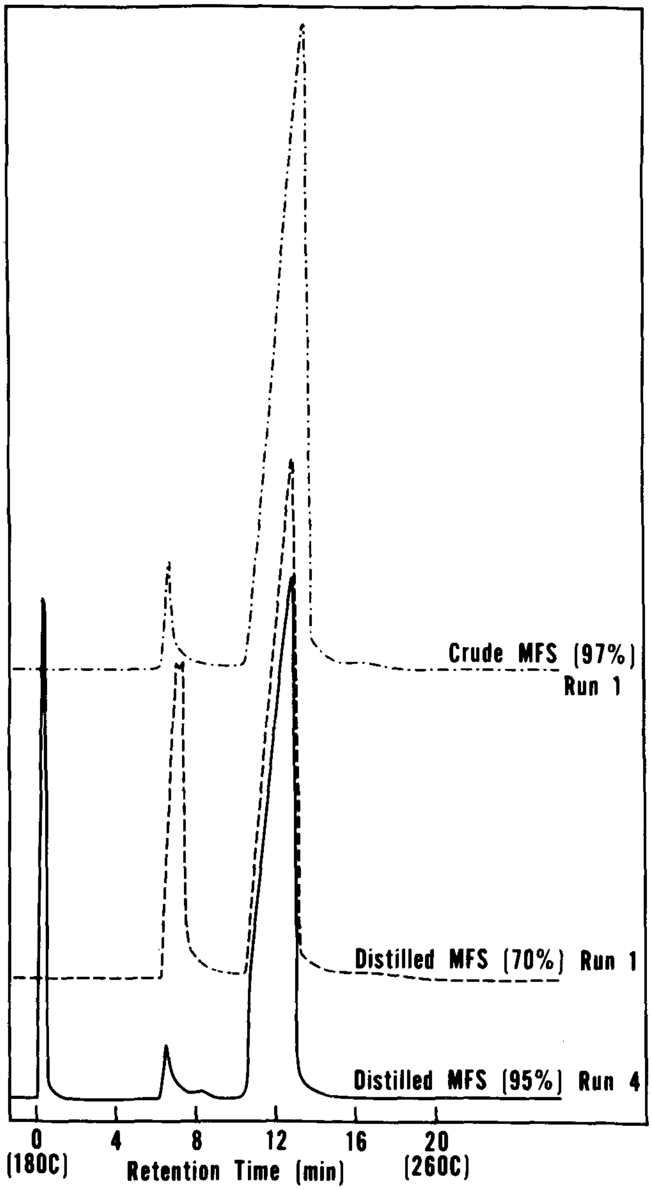

FIG. 3. Gas chromatograms comparing crude methyl formylstearate with 2 distilled products.

## MATERIALS

MO was prepared from Hercules Pamolyn 100, a commercial-grade oleic acid, by direct esterification with methanol and sulfuric acid. The washed reaction product was vacuum distilled to give 98% pure MO. The 1:1 mixture of hydrogen and carbon monoxide was purchased from Matheson Gas Products. TPP came from Strem Chemicals, Inc.

The ARC was prepared as indicated in step 4 of the process (Fig. 1); i.e. distillation residues from previous work, which contained a known concentration of rhodium, were resupported on alumina. This alumina was obtained from Engelhard and is the same as that used for its rhodium-on-alumina catalyst.

## EQUIPMENT

The hydroformylation reactions were carried out in a 2-liter 316SS rocker-shaker autoclave from Autoclave Engineers. The autoclave was equipped with an external cooling jacket and had a pressure rating of 3000 psi at 300 C.

The kiln used to reactivate spent catalyst (Fig. 2) was constructed in-house. The vessel was made from a 6-in. long section of 3 in. tubing. The bottom of the kiln was cut from 0.125 in. plate and welded to one end of the tube. The flange and cover were also 0.125 in. plate and were machined to mate. The cover was fastened to the body with six 0.125 in. bolts and wing nuts. A 4.250 in. length of 1 in. cold-rolled steel was attached to the base of the vessel to act as a bearing surface and drive shaft. A 15 in. length of 1 in. pipe was welded to the cover to permit introduction of an air tube and the escape of combustion products. This pipe also served as an axis to support the other end of the rotating vessel. Three 5.750 in. lengths of 0.375 in. rod were used inside the vessel to facilitate mixing. All wetted parts were constructed of 316 stainless steel. The furnace was fashioned of 16 gauge steel and covered with 0.5 in. asbestos board. Three baffled ports large enough to accept the top of a Fisher burner were welded into the base of the furnace at regular intervals. A port was also placed in the upper half of the furnace to act as a chimney. Bronze bearings made from 1 in. thick stock were fastened to the outside of both ends of the furnace. The vessel was rotated within the furnace at 12 rpm by a small gear head motor.

## PROCESS

The quantitative data in Figure 1 are from run 4 and are

TABLE I

Hydroformylation of MO.[a] Effects of Cycling Reactivated Rhodium Catalyst

| Run | Reaction time, min | Conversion, % | MFS, g | Purity, %[b] | Residue, g | Rh, mg[c] | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Residue | Support | Total |
| 1 | 40 | 99 | 506 | 70 | 23.8 | 204 | --- | --- |
| 2 | 43 | 97 | 523 | --- | 14.5 | 186 | --- | --- |
| 3 | 41 | 99 | 525 | 90 | 22.2 | 190 | --- | --- |
| 4 | 43 | 96 | 527 | 95 | 18.0 | 180 | --- | --- |
| 5 | 48[d] | 97 | 527 | 93 | 22.4 | 182 | 26 | 208 |
| 6 | 51 | --- | 528 | 96 | 18.1 | 161 | --- | --- |
| 7 | 46 | 96 | 530 | 95 | 16.5 | 174 | --- | --- |
| 8 | 46 | 96 | 529 | 94 | 19.1 | --- | --- | --- |
| 9 | 55 | 96 | 532 | 93 | 18.4 | 160 | --- | --- |
| 10 | 56 | 97 | 526 | 93 | 15.1 | 145 | 36 | 181[e] |
| Control | 160 | 98 | 532 | 97 | 14.6 | 102 | 141 | 243[f] |

[a] For each run, 500 g of 98% pure MO and 2.5 g of TPP were used. MO = methyl oleate; TPP = triphenylphosphite; MFS = methyl formylstearate.

[b] Impurities are unconverted MO, 2% methyl stearate in starting material and decarbonylation products (MO and methyl stearate).

[c] Initial catalyst charge was 16.9 g of $Al_2O_3$ containing 250 mg Rh.

[d] Reaction temperature was 117 C for this run as compared to 120-122 C for the other nine runs.

[e] 181 mg does not reflect the 16 mg lost in analysis of residues or the 9 mg recovered by a second distillation of the MFS.

[f] Fresh commercial 5% Rh (5 g) on $Al_2O_3$ catalyst was used for the control run.

considered typical; Table I contains quantitative data on the individual runs. The descriptive material and quantitative data in the following 4 sections are from run 1.

### Step 1–Hydroformylation

MO (500 g), ARC (16.9 g containing 0.25 g Rh), and TPP (2.5 g) (recent studies have indicated that as much as 1% TPP may be required for the initial reaction) were charged to the autoclave. The reactor was first flushed with a 1:1 mixture of $H_2$ and CO, then pressurized with the same mixture to 500 psig and heated with agitation to 100 C at 2 C/min. The pressure increased to ca. 660 psig during heat-up. When the temperature reached 100 C, the rapid pressure drop indicated an initial reaction. The pressure was increased to 900 psig and heating continued to 120 C. Gas uptake was very rapid, and pressure was cycled manually between 850 and 900 psig. Reaction temperature was maintained during this period without benefit of external heat. After ca. 20 min gas absorption began to slow down noticeably, and the reaction was complete within 40 min after the initial uptake.

### Step 2–Filtration

The autoclave was cooled and the excess pressure vented. The contents of the opened vessel were siphoned into a Buchner funnel and filtered under vacuum through Whatman qualitative filter paper. To obtain an accurate material balance, the autoclave was rinsed with acetone and this rinse in turn used to wash the spent catalyst support (SCS) in the filter funnel. The filtered acetone solution was stripped under vacuum and the residue combined with the main filtrate. The combined filtrates weighed 549.4 g. The conversion of MO to MFS was nearly quantitative as indicated by gas liquid chromatography (GLC) (Fig. 3). The SCS (17.4 g) and filter paper were transferred to the kiln for step 4.

TABLE II

Estimate of Fixed Capital Investment for a Plant Producing 2 Million lb MFS (95% Purity) Annually[a]

| Item | Cost |
|---|---|
| Equipment delivered: | |
| 2 Reactors with agitator and jacket, 650 gal, 900 psig | $100,000 |
| Filter, plate and frame | 5,000 |
| Distillation unit complete with all accessories | 90,000 |
| Kiln for catalyst recovery, electrically heated | 10,000 |
| Storage tanks for methyl esters and product | 30,000 |
| Pumps, scales and miscellaneous equipment | 5,000 |
| Total delivered equipment cost | $240,000 |
| Total erected equipment cost | 600,000 |
| Building | 30,000 |
| Estimated fixed capital investment | $630,000 |

[a] Basis: 250 operating days/year, 8 hr/day.

### Step 3–Distillation

The filtrate was transferred quantitatively to a 1-liter round-bottomed flask fitted with a 4 in. jacketed Vigreux column. Vacuum distillation, details of which are not typical of later runs, began at a pot temperature of ca. 200 C and a head temperature of 190-195 C. As the pot temperature rose from 200 to 225 C, the pressure increased from 1 to ca. 2 mm with considerable smoking. The residue (23.8 g) containing the SRC was dark and viscous. The distillate (506 g) was water white but had undergone significant decarbonylation to methyl stearate and MO as indicated by GLC (Fig. 3), as well as by the loss in combined wt of distillate and residue (529.8 g) as compared

TABLE III

Estimated Processing Costs for a Plant Producing 2 Million lb MFS (95% Purity) Annually[a]

| Item | Daily cost, dollars | Cents/lb, MFS |
|---|---|---|
| Raw materials: | | |
| Synthesis gas, 26,000 $ft^3$/day, $0.75/M $ft^3$ | $ 19.50 | 0.2 |
| TPP,[b] 38 lb/day, $0.35/lb | 13.30 | 0.2 |
| Catalyst, 5% Rh on $Al_2O_3$, 1.52 lb/day, $177/lb | 269.04 | 3.4[c] |
| | 301.84 | 3.8 |
| Utilities: | | |
| Steam, 7000 lb/day, $0.75/M lb | 5.25 | |
| Water, 20,000 gal/day, $0.15/M gal | 3.00 | |
| Gas, 10,000 $ft^3$/day, $0.60/M $ft^3$ | 6.00 | |
| Electricity, 900 kwh/day, $0.015/kwh | 13.50 | |
| | 27.75 | 0.3 |
| Labor and supervision: | | |
| Operators, 20 man-hr/day, $5.50/hr (including overhead) | 110.00 | |
| Supervision, 20% of operator costs | 22.00 | |
| | 132.00 | 1.7 |
| Maintenance: | | |
| Equipment, 6%/yr on $600,000 | 144.00 | |
| Building, 2%/yr on $30,000 | 2.40 | |
| | 146.40 | 1.8 |
| Fixed charges: | | |
| Depreciation | | |
| Equipment, 10%/yr on $600,000 | 240.00 | |
| Building, 5%/yr on $30,000 | 6.00 | |
| Taxes and insurance, 3%/yr on $630,000 | 75.60 | |
| | 321.60 | 4.0 |
| Miscellaneous factory supplies and expense | 21.96 | 0.3 |
| General plant overhead | 139.20 | 1.8 |
| Estimated daily cost, total | $1090.75 | |
| Estimated processing costs, cents/lb product | | 13.7[d] |

[a] Basis: 250 operating days/year, 8 hr/day.

[b] TPP = triphenylphosphite.

[c] Represents cost for 2% catalyst makeup.

[d] Cost for MO not included.

to the initial charge (549.4 g).

Even though the distillation data collected on the first run of the series are atypical, the actual data are included for the sake of continuity. In a typical run (Fig. 3 and Table I) MFS is distilled at a head temperature of ca. 185 C at 0.3-0.5 mm. Decarbonylation is minimal 1-4%, and 525-530 g of distilled MFS are obtained from 550 g of filtered reaction product.

### Step 4–Catalyst Reactivation

A 0.1801 g sample of the SRC residue was analyzed for rhodium (Rh) by atomic absorption (7) and found to contain 8.57 mg Rh/g. The entire SRC residue containing 204 mg of Rh was quantitatively transferred to the kiln (Fig. 2), in which had been placed the SCS (17.4 g) along with the filter paper used in step 2. The furnace was heated with one Fisher burner to ca. 280-300 C. The front of the furnace was elevated slightly so that any liquid condensing in the tube would reflux back into the kiln and be charred. After 1 hr or when there was no more evidence of liquid condensate, a second burner was lit and the temperature raised to ca. 620 C. A slow stream of air was introduced into the kiln by means of a 0.250 in. tube inserted through the open end of the kiln. Heating was continued for 2 hr. The cooled ARC (16.88 g) was recycled to step 1 of the process.

## RESULTS AND DISCUSSION

Quantitative data are recorded in Table I for a series of 10 runs in which the same rhodium catalyst was reactivated and recycled as described.

Presumably, the ARC in this series is in oxide form and is much more active than commercial Rh on alumina. In a control run, at the same Rh level and under identical conditions, a commercial catalyst required 2 hr and 40 min to convert MO completely to MFS as compared to 40 min for ARC. Roasting the commercial Rh on alumina for 3 hr at 600 C in the kiln gave a catalyst that was almost as active as the ARC.

There is an obvious loss of Rh from run to run. However, no makeup catalyst was added because activity remained at a high level as indicated by the continued good conversion of MO to MFS. The reaction time required for conversion increased from 40 to 56 min as the catalyst level decreased from 250 mg to 181 mg.

The analyses of the residues required an average of 1.8 mg Rh each or a total of 16 mg. A second distillation of the MFS from all runs yielded an additional 9 mg. This small quantity of Rh does not indicate limited volatility but probably entrainment during the original distillations. Therefore, a total of 206 of the original 250 mg of Rh is accounted for. The remaining 44 mg loss probably comes from two sources, handling and air entrainment. With continued use, the catalyst support becomes increasingly fine and cannot be removed from the kiln without some dusting; when dealing with such small quantities, handling losses result. Dusting is also a problem in the roasting operation itself. Even a small stream of air passed over the hot agitated catalyst entrains catalyst particles, and no provisions were made to arrest them.

There appears to be a direct relationship between the amount of soluble Rh in the crude reaction product and catalyst activity as indicated by reaction time. Noteworthy is run 6 that required 51 min and showed only 161 mg Rh in the residue. The observation is substantiated further by the control run in which only ca. 41% (102 mg) of the Rh in the less active commercial catalyst (2 hr 40 min reaction time) was solubilized. The reason for the results in run 6 and for other small irregularities shown in Table I is that temperature control of a kiln heated by Fisher burners is difficult and is not reproducible. Temperature variation could produce catalysts of slightly different activities.

Vacuum distillation of crude MFS containing SRC resulted in appreciable decarbonylation in the first run (Table I and Fig. 3). This decomposition might have been caused by heating the pot too rapidly or by the high concentration and high activity of the soluble catalyst; however, it ceased to be a significant problem in subsequent runs. If the problem is one of catalyst concentration, it could be avoided by going to lower levels for hydroformylation (e.g. run 10) since reasonable catalyst activity is maintained at these lower levels.

### Preliminary Cost Estimate

The hypothetical plant upon which a preliminary cost estimate is based has an annual capacity of 2 million lb of MFS (95% purity) when operations are conducted 250 days a year, 8 hr/day. Presumably, the plant would operate as an adjunct to an existing vegetable oil processing plant.

Estimated fixed capital investment for a battery limits installation is $630,000 (Table II). Estimated processing costs in the plant, not including the cost for MO, are 13.7 cents/lb of MFS with 95% purity (Table III). Items included in the processing costs are raw materials other than MO, utilities, labor and supervision, maintenance, fixed charges, miscellaneous factory supplies, and expenses and general plant overhead.

Operating procedures in the plant would follow, in general, the process as depicted in the flow chart (Fig. 1). Predicted plant yield for the process is ca. 105 lb of MFS (95% purity)/100 lb MO (98% purity). Since the rhodium catalyst which is used in this process is priced at $175-$180/lb of material containing 5% rhodium on alumina, efficient recovery of the catalyst is vital to the economics of the process. Value of the 76 lb catalyst for the initial day's operation in the hypothetical plant is ca. $13,500.

In laboratory experiments, total catalyst loss per run averaged ca. 1.8% during 10 runs with the recovered catalyst from one run being recycled to the next run. On a plant scale, catalyst loss from physical or mechanical losses would be expected to be less than that in laboratory experiments as pointed out previously in the discussion. Nevertheless, calculations for this estimate were based on a catalyst makeup of 2%. It is difficult to predict the actual number of times the catalyst can be recycled to the process without affecting the efficiency of the operation and with no catalyst treatment other than that described in this paper. However, laboratory results indicate that it should be possible in a plant to recycle the catalyst for many more runs than the 10 runs reported for laboratory studies.

## ACKNOWLEDGMENTS

Hydroformylation reactions were carried out by R.L. Reichert.

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