Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Distillation of Reactive Methyl Glyoxylate-Methyl Glycolate Mixtures

D. R. Cova[a]; J. M. Thorman[a]
[a] Detergents and Phosphates Division, Monsanto Company, Louis, MO

To cite this Article Cova, D. R. and Thorman, J. M.(1990) 'Distillation of Reactive Methyl Glyoxylate-Methyl Glycolate Mixtures', Separation Science and Technology, 25: 13, 1981 — 1991
To link to this Article: DOI: 10.1080/01496399008050438
URL: http://dx.doi.org/10.1080/01496399008050438

SEPARATION SCIENCE AND TECHNOLOGY, 25(13-15), pp. 1981-1991 (1990)

DISTILLATION OF REACTIVE METHYL GLYOXYLATE-METHYL GLYCOLATE MIXTURES

D. R. Cova and J. M. Thorman
Detergents and Phosphates Division
Monsanto Company
800 N. Lindbergh Blvd.
St. Louis, MO 63167

ABSTRACT

A process for refining methyl glyoxylate produced via air-oxidation of methyl glycolate is described. This is a unique separation as methyl glyoxylate reacts reversibly with several impurities in the reaction effluent (i.e., water, methanol and methyl glycolate). Separating water and methanol is accomplished using differences in volatilities and reaction equilibria. Azeotropic distillation is of particular importance in reducing water to specification levels. Separating methyl glycolate utilizes the effect of system pressure on volatility and reaction equilibrium. Recovery of methyl glycolate for recycle to oxidation is accomplished by passage through low-retention time stills.

INTRODUCTION

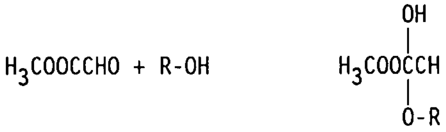
Methyl glyoxylate (Gx) can be produced by the air oxidation of methyl glycolate (Gc) as shown in Eq. (1):

$$\underset{\text{(Gc)}}{H_3COOCCH_2OH} + 1/2\ O_2 \qquad\qquad \underset{\text{(Gx)}}{H_3COOCCHO} + H_2O \qquad (1)$$

Our purpose in this work was to develop a process for a non-phosphate detergent builder based on a polymer of glyoxylic acid. This involved reacting Gc to form Gx, refining the Gx into suitable monomer, polymerizing the monomer, and processing the polymer into final form. The study reported here is concerned with refining Gx and recovering unreacted Gc.

Crude Gx from oxidation contains considerable quantities of water, methanol, and unreacted Gc, plus traces of organic acids. All must be removed to low levels to make suitable monomer. Any compound containing the -OH moiety is a chain initiator in the polymerization area. Desired polymer chain lengths of about 100 necessitated reducing water, methanol, and Gc levels in Gx monomer such that the molar ratio of total -OH to Gx was <0.01. While this process was never commercialized, the problems encountered in refining are (and have been) of interest to the technical community (1,2,3).

Gx is very difficult to purify, owing to its reactive nature. It polymerizes upon standing. It also reacts reversibly with any compound containing -OH groups to form hemiacetals (hydrate in the case of water) as shown in Eq. (2).



$$H_3COOCCHO + R\text{-}OH \qquad H_3COO\overset{\displaystyle OH}{\underset{\displaystyle O\text{-}R}{C}}H \qquad (2)$$

where R = H-, H_3C- or $H_3COOCCH_2$-

This complicates the refining of reactor effluent containing water, methanol and Gc. For example, distilling a mixture of methanol and Gx produces some pure methanol or Gx (depending on original concentrations), but most of the Gx will be recovered as a mixture of Gx and the Gx-methanol hemiacetal. The same holds true for Gx mixtures with water and Gc.

EXPERIMENTAL

ANALYTICAL

The hemiacetals are very labile and their concentrations in a mixture depend upon the concentrations of original components and the mixture condition (temperature, pressure, degree of equilibrium of the mixture). Thus, analysis of actual content would have to be in-situ, as any change in mixture condition or any time required for analysis would bring about composition change. We had limited success in using nuclear magnetic resonance (NMR) for this purpose. NMR was used to determine equilibria for the different hemiacetals, but the instrument was too limited for use as a general analytical tool. Gas chromatography was generally used as the preferred analytical tool. Hemiacetals and hydrates broke down within the heated injection port of the gas chromatograph into original components so that this tool was useful in determining purity but not in determining the presence or quantity of hemiacetals and hydrates. These could only be inferred from the behavior of the mixtures in processing. The vapor-liquid equilibrium data shown in Fig. 1 are based on gas chromatographic analyses, as are the weights given in the material balance. Therefore, wherever Gx, Gc, methanol or water compositions are referred to in Fig. 1 and the material balance, what is meant is the total of both the free compound and that tied up in the hemiacetal or hydrate.

VAPOR-LIQUID EQUILIBRIA

Vapor-liquid equilibria for the systems, Gx-Gc, Gx-methanol and Gx-water were determined in a Gillespie-type recirculating still (4). Since there was a possibility that reaction kinetics could have had an effect on the data, some points were repeated using a different technique. This was the dynamic flow method in which nitrogen gas was saturated with equilibrium vapor by flowing through three thermostatted vessels containing a liquid mixture (5). There was little difference in the data.

FRACTIONATION

Fractionation was generally carried out in 1- and 2-in diameter Oldershaw columns operated in the continuous mode. Thermosyphon-type reboilers were designed with low retention times to reduce thermal degradation of the materials.

RESULTS AND DISCUSSION

WATER AND METHANOL REMOVAL

Vapor-liquid equilibrium curves for the Gx-Gc, Gx-water and Gx-methanol systems shown in Fig. 1 are very similar to those of systems displaying high-boiling azeotropes (HCl-water, HF-water, chloroform-acetone, etc.). Here, however, chemical kinetics influence the volatilities. Note that changes in pressure have little effect on the "azeotrope" compositions of systems involving water and methanol.

Analysis of equilibrium binary mixtures of Gx with methanol, Gc and water at various temperatures by nuclear magnetic resonance gave an indication of the reaction equilibrium and free energy. From this, relative bonding strength could be deduced. The hemiacetal with methanol was the strongest, next Gc, while the hydrate with water was the weakest. Both methanol and water are more volatile than Gc, so that under distillation conditions there is a tendency to drive off these lower boilers in preference to Gc. Furthermore, reaction equilibria comes into effect in that the presence of Gc in the system forces more methanol and water to boil out of the system by replacing them in their reaction with Gx. The data in Table 1 show this effect.

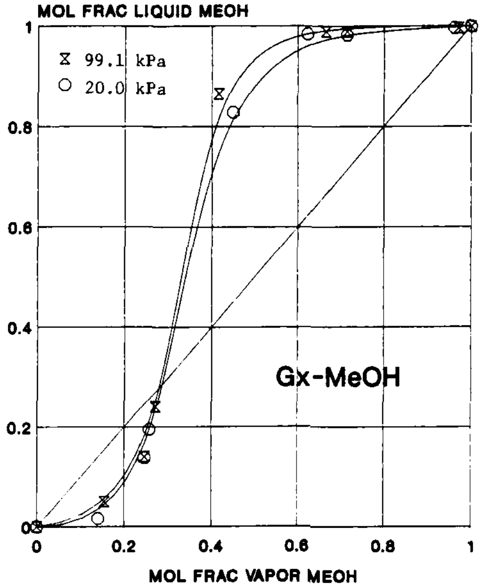


Figure 1a. Vapor-Liquid Equilibria for GX-MeOH

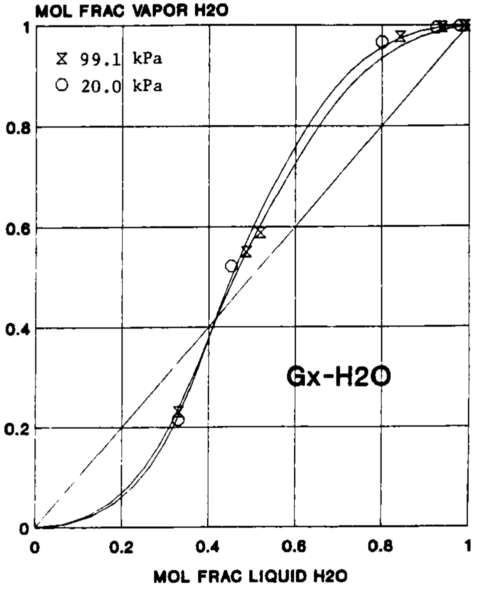


Figure 1b. Vapor-Liquid Equilibria for GX-H2O

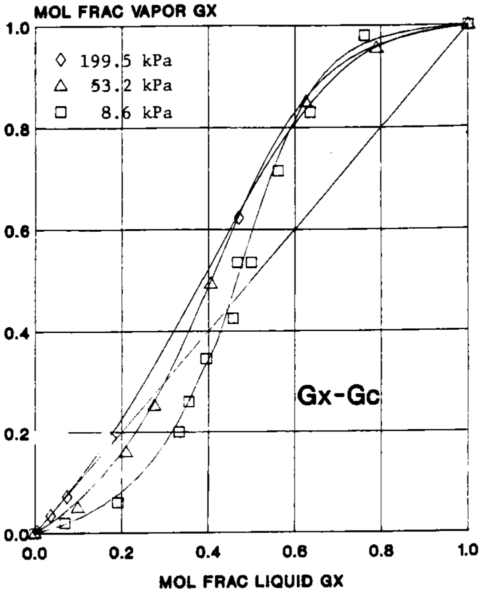


Fig. 1c Vapor-Liquid Equilibria for GX-GC

A substantial amount of methanol and water can be removed in this way, but remaining levels still exceed strict product specifications. Furthermore, downstream chemical degradation produces more water, and hydrolysis produces more methanol. Some means of reducing these levels further was required. Removing the remaining methanol was relatively easy. Once the Gc was removed, methanol could be separated from the Gx as the higher boiling hemiacetal (see Fig. 2). Water was a much more difficult problem, because of the weak bonding. Water tended to distribute throughout the entire distillation column. Before considering this problem, the separation of Gc is described.

METHYL GLYCOLATE REMOVAL

The vapor liquid equilibrium curves for the Gx-Gc system (Fig. 1) show that system pressure has a large effect on the composition of the "azeotrope". This composition varies from a high Gx level at low pressures to low levels at higher pressures and almost disappears at 202. kPa (2 atm). This phenomenon allows an easy separation between Gx and Gc. By distilling at atmospheric pressure most of the Gx in the column feed is recovered free of Gc while producing a bottoms stream depleted in Gc. Downstream in the process purified Gc is recovered for recycle from this bottoms stream by distilling at high vacuum. This is described in a later section.

TABLE 1

Extent of Water and Methanol Removal in Low-Boiler Column

Gc:Gx wt ratio	Bottoms Composition Water, wt%	Methanol, wt%
50:50	0.6	1.0
40:60	1.2	1.1
18:82	4.3	1.9

PRODUCING SPECIFICATION-GRADE METHYL GLYOXYLATE

Simple fractionation to remove Gc produced Gx containing levels of water and methanol above specifications. Some means was necessary to reduce these levels. Methanol could be readily removed by fractionation. Water was much more difficult to remove.

Contacting Gx with anhydrous salts was unsuccessful in reducing water levels. Contacting with phosphorus pentoxide or polyphosphoric acid reduced the water level but was uneconomical. Contacting with zeolite molecular sieve also reduced water levels but was uneconomical because of low capacity for water under the conditions of operation. The most economical solution was the use of an entrainer to strip out water during the separation of Gx from Gc (Gx monomer column) and of Gx from methanol (finishing column) (6). Choice of a suitable azeotroping agent involved several criteria. These included: 1) process compatibility, 2) forming a two-phase system with water, 3) low solubility of water in the agent, 4) water level in azeotrope significantly greater than water solubility in agent, 5) boiling point less than 100°C at 101. kPa (1 atm), 6) agent non-reactive, and 7) totally miscible in Gx. Identifying one workable agent led to a class of suitable azeotroping agents based upon the paper by Godfrey (7). Our choice for operational reasons was methylene chloride. Fig. 2 shows the mode of operation.

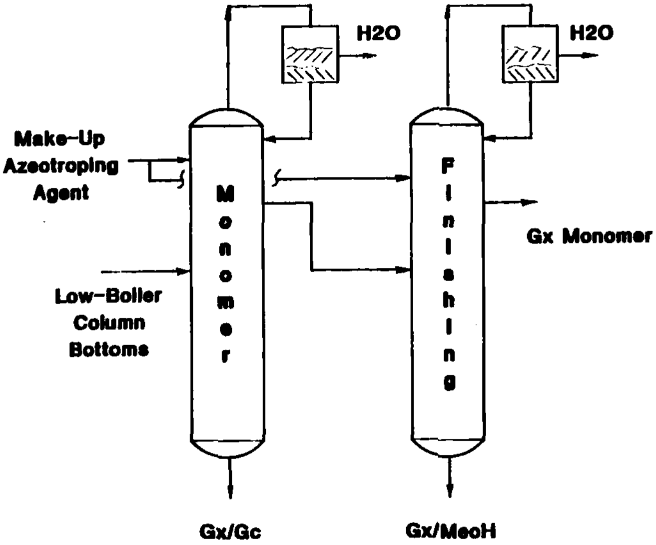


Fig. 2 Azeotropic Distillation

In the preferred mode of operation in Fig. 2, a second column is shown. This is the finishing column where methanol was removed as the high-boiling hemiacetal. Entrainer was also used here to remove more water from the Gx monomer. With this mode of operation -OH levels (from water, methanol and Gc) were well below that required for suitable monomer. Attempts to combine these two columns into one failed.

RECOVERY OF METHYL GLYCOLATE

Bottoms from the Gx monomer column contained about 20% Gx and 80% Gc. Gx levels could be reduced by operation at higher pressures (202. kPa or higher), but the higher temperatures involved could lead to increased chemical degradation in the reboilers. Operation at atmospheric pressure was preferred. It was necessary to purify Gc before recycling it back to the oxidation area. Distillation at reduced pressure raises the level of Gx combined with Gc in the hemiacetal. This frees up Gc which is lower boiling than the hemiacetal and can be distilled off. First it was necessary to cool the bottoms from the Gx refining column and hold it in a surge tank to allow formation of the hemiacetal. Low retention time stills were used to maximize the separation. The operating pressure selected was 1.33 kPa (10 mm Hg). With a single wiped film still (retention time

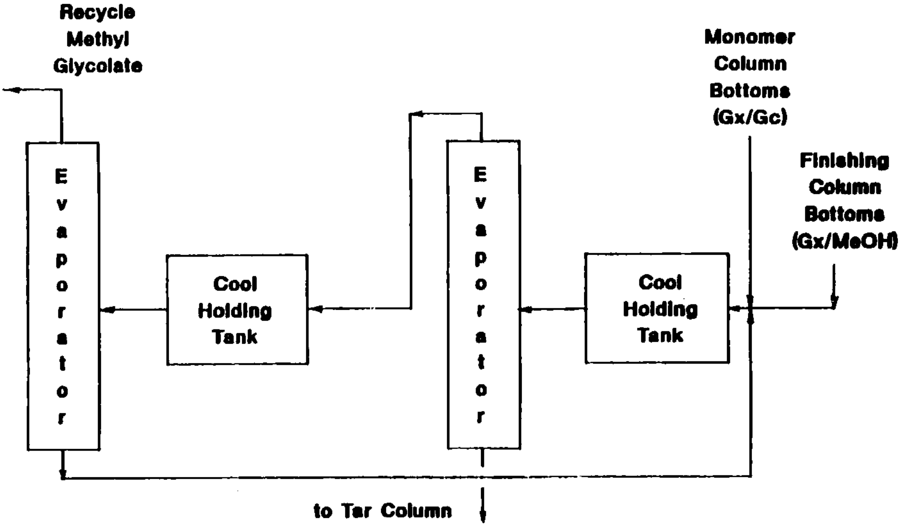


Fig. 3 Methyl Glycolate Recovery

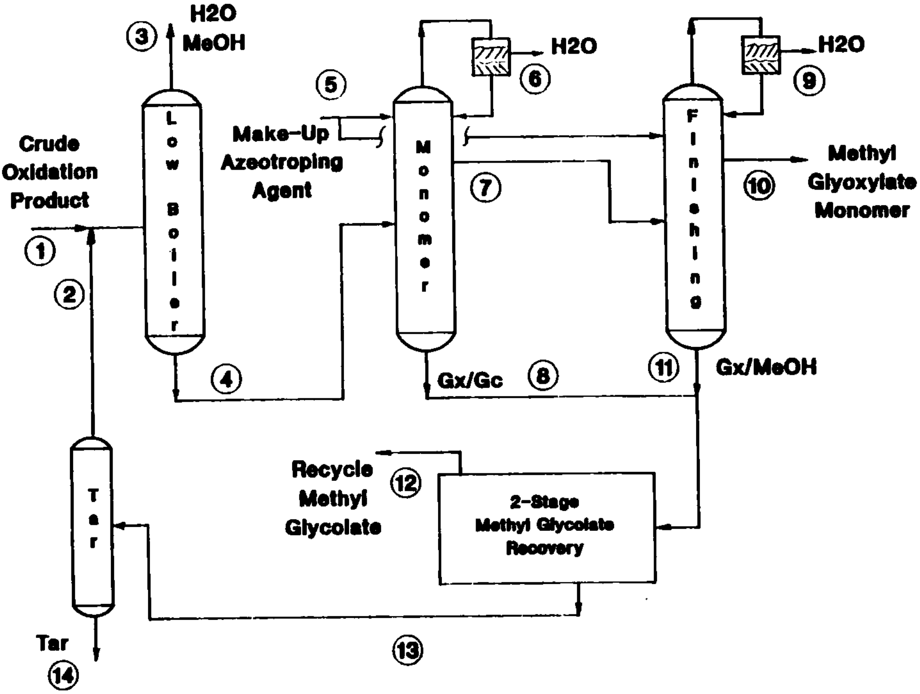


Fig. 4 Overall Process

Table 2. Process Balance and Conditions

Component	Crude Feed (1)	Tar OH (2)	LB Dist (3)	LB Bot (4)	$MeCl_2$ MakeUp (5)	Monomer H_2O (6)	Monomer SD (7)	Monomer Bot (8)	Finish H_2O (9)	Finish SD (10)	Finish Bot (11)	Recycle Gc (12)	Tar Feed (13)	Tar Bot (14)
H_2O	19.7	0.2	17.4	2.4	---	1.3	1.1	---	0.5	0.1	0.5	0.3	0.2	---
MeOH	5.7	9.3	5.1	9.9	---	0.1	9.2	0.7	<0.1	---	9.1	0.4	9.3	---
Gx	105.8	132.3	---	238.2	---	---	165.6	72.6	---	98.3	67.2	1.1	138.7	6.4
Gc	151.7	107.4	---	259.1	---	---	5.0	254.1	---	---	5.0	145.3	113.8	6.4
$MeCl_2$	---	---	---	---	1.6	<0.1	1.6	---	<0.1	1.6	---	---	---	---
Tar	2.9	---	---	2.9	---	---	---	2.9	---	---	---	---	2.9	2.9
Total	285.8	249.2	22.5	512.5	1.6	1.4	182.5	330[illegible]	0.6	100.0	81.8	147.1	264.9	15.7
Temp, C	15	68	33	97	25	15	116	153	15	116	135	50	55	150
Pressure, kPa	101	6.65	6.65	11.7	---	101	104	109	101	103	106	1.46	1.46	7.32

in seconds) it was possible to obtain a distillate with 98% Gc concentration and a bottoms with 61% Gc. For economic reasons a system of two stills with 3 to 15 minutes retention time in each stage was used. This gave a distillate of 98.5 to 99% Gc and a bottoms of 61 to 65% Gc. The flow diagram is shown in Fig. 3. Due to the kinetics of hemiacetal formation and dissociation these simple stills provided as good or better a separation as could be obtained in a fractionation column (8).

TOTAL PROCESS

The total flow diagram for the refining operation is shown in Fig. 4. Material balance and operating pressures and temperatures are given in Table 2. Besides the operations discussed above, a high boiler removal column was added to clean up column bottoms flowing back into refining.

ACKNOWLEDGEMENTS

The contributions to this work of D. R. Dyroff, Y. Chou, D. J. Wiese and P. C. Schacht are gratefully acknowledged.

REFERENCES

1. T. Kakimoto, Y. Kawase and K. Hirata, Japanese Patent 61 50,941 (1986); Chem Abstr, 105, 78,528 (1986).

2. D. R. Dyroff, Y. Chou and D. R. Cova, U.S. Patent 4,502,923 (1985).

3. Y. Christidis, U.S. Patent 4,156,093 (1979).

4. E. Hala, et al, Vapour-Liquid Equilibrium, 2nd Ed., Pergamon, 1967, p. 300.

5. C. S. Robinson and E. R. Gilliland, Elements of Fractional Distillation, 4th Ed., McGraw-Hill, New York, 1950, p.6-7.

6. D. R. Cova and J. M. Thorman, U.S. Patent 4,820,385 (1989).

7. N. B. Godfrey, "Solvent Selection Via Miscibility Number," Chemtech, 2, 359 (1972).

8. D. R. Cova and J. M. Thorman, U. S. Patent 4,867,849 (1989).