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Synthesis of Propionic Anhydride and Propionic Acid

Optimum conditions have been developed for making propionic anhydride from ethylene, carbon monoxide, and propionic acid and propionic acid from ethylene, carbon monoxide, and water in any desired ratio on a semiworks scale

ALTHOUGH many syntheses have been reported for organic acids and anhydrides, relatively few have been attractive for industrial development. In many cases the need for corrosive catalysts, such as hydrochloric acid, or for expensive reagents, such as acetic anhydride, has been a major difficulty. However, studies in this laboratory (4-7) have shown that noncorrosive nickel carbonyl is an effective catalyst for the synthesis of propionic acid from inexpensive ethylene, carbon monoxide, and water, and of propionic anhydride from ethylene, carbon monoxide, and propionic acid.

Tests in small closed vessels indicated good reactivity at pressures of 300 to 800 atm. and temperatures near 300° C. Conversions and yields were promising enough to justify detailed study of these reactions in semiworks apparatus under continuous flow conditions.

Semiworks Study

Carbon monoxide was prepared by cracking methyl formate, stored at 1 atm. over water, and compressed by a five-stage Hofer compressor (7E). The compressed gas was circulated through empty traps and traps packed with silica gel to remove oil, through a hot tube packed with reduced copper oxide to remove oxygen, and through traps packed with stick caustic to remove carbon dioxide and water. The purified gas contained more than 99% carbon monoxide with traces of oxygen, nitrogen, and hydrogen.

Commercial "medicinal grade" ethylene was compressed to about 1200 pounds per square inch by an Ingersoll-Rand compressor (4E) and purified by a system of traps similar to that used for carbon monoxide. The compressed, purified gas was then condensed at about -10° C. and injected into the high-pressure system by a liquid pump (2E). For some experiments when flexibility was not an important operating objective, ethylene was mixed with carbon monoxide at 1 atm. and the mixture was compressed and purified by the system first used for carbon monoxide alone. In either case the purified ethylene

component contained 97.5 to 99% ethylene, as much as 1.5% hydrogen, and lower hydrocarbons to make 100%.

Solutions of nickel carbonyl in 99% propionic acid or of nickel propionate in aqueous propionic acid were prepared in a closed stainless steel system and injected by a stainless steel pump of the Hofer type (3E). The reagents and the apparatus were purged and blanketed with nitrogen or waste gases from the converter to keep oxygen concentrations at low levels.

The compressed gases or gas mixture and the liquid feed were metered into the high-pressure system by operating the pumps at controlled rates, mixed in tees, and allowed to flow downward through the converter at a slight angle.

Preliminary experiments had shown that neither copper nor stainless steel is sufficiently resistant for extended service in contact with the hot reaction gases. Therefore, silver-lined equipment was used, even though deterioration in the mechanical properties of silver at high temperatures limited most tests to temperatures no higher than 300° C. In most experiments one of two converters was used. The longer consisted of 270 feet of steel tubing, 5/8 inch in outside diameter and 1/4 inch in inside diameter, silver-lined to a net inner diameter of 3/16 inch and having a volume of 0.05 cubic foot. Temperature was controlled by a jacket containing boiling liquid, usually Dowtherm A. The second converter consisted of three sections of 1 1/2 x 5/8 inch steel tubing silver-lined to a net inner diameter of 9/16 inch.

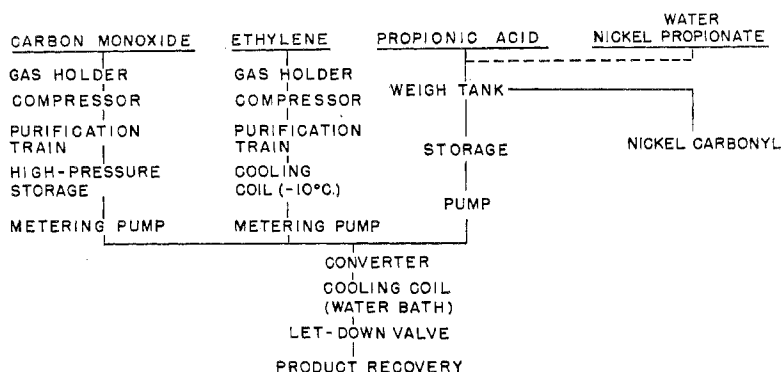
Each section was equipped with a separately controlled jacket of boiling liquid. The first section was 10 feet long and was usually operated as a preheater. The second and third sections were 17 1/2 feet long with a combined volume of 0.06 cubic foot. In a few experiments, a vertical 10 foot silver lined tube 9/16 inch in inside diameter, similar to the preheater section, was used as a converter both with and without a packing of 1/4 inch copper rivets.

The mixture leaving the converter was cooled in a 20-foot coil of silver-lined tubing, 1/8 inch in inside diameter, immersed in a water bath and let down to the low-pressure separator at 10 pounds per square inch and then to the product refining system. The products were analyzed and purified by standard techniques.

Discussion

Special experiments, including tests of upward flow in place of the usual downward flow, showed that the fluid in the converter forms a single homogeneous phase under the conditions tested. Other special experiments with the copper packing indicated that reaction rates are not affected by converter area.

The reactions are only slightly sensitive to impurities. At the usual concentration of about 10 p.p.m., oxygen has no perceptible effect. Concentrations of 200 to 500 p.p.m. reduce reaction rates significantly. Hydrogen introduced as an ethylene impurity reacts



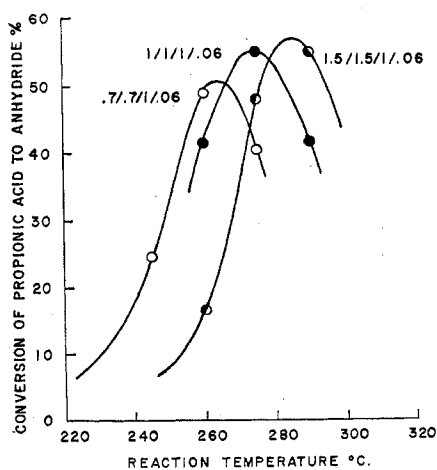


Figure 1. Effect of temperature on conversion at 600 atm.

Complex fractions denote molar feed ratios $\text{CO}/\text{C}_2\text{H}_4/\text{C}_2\text{H}_5\text{COOH}/\text{Ni}(\text{CO})_4$

with ethylene to form ethane and with ethylene and carbon monoxide to form diethyl ketone. Conversion to diethyl ketone is almost unaffected by increases in hydrogen concentration and conversion to ethane is only slightly affected.

The only substantial yield losses are to ethane, diethyl ketone, and a high-boiling residue of unidentified composition. In most cases, the total loss is equivalent to 2 to 6% of available ethylene.

The experimental value for conversion of acid to anhydride provides an effective measure of catalyst activity in the synthesis of anhydride. As temperature is increased, this conversion passes through the sharp peaks shown in Figure 1. Because conversion at these peaks may be less than the maximum or equilibrium conversion, it is called the optimum conversion. The temperature at which this optimum occurs is called the optimum temperature. These curves show that increases in carbon monoxide concentration cause increases in optimum temperature. When the operating temperature is less than the optimum, the nickel carbonyl in the reaction mixture

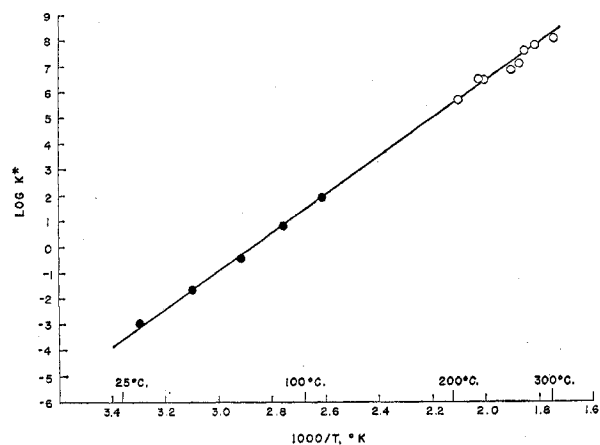


Figure 2. Equilibrium constants for system nickel-carbon monoxide-nickel carbonyl

is relatively stable; when greater than the optimum, the synthesis reactions produce substantial quantities of ionic nickel and, in extreme cases, nickel dust. These results suggest that the activity of the catalyst varies significantly with the stability of nickel carbonyl.

For any feed or reaction mixture under any experimental conditions an index of the stability of nickel carbonyl can be obtained by comparing the maximum possible partial pressure of nickel carbonyl with the maximum available partial pressure. The maximum possible pressure is established by equilibrium with the actual partial pressure of carbon monoxide in the mixture and with a trace of metallic nickel. This can be computed from the usual expression for the equilibrium constant

$$K^* = P_{\text{CO}}^4 / P_{\text{Ni}(\text{CO})_4} \quad (1)$$

by imposing the condition that the actual and equilibrium pressures of carbon monoxide are equal.

$$P_{\text{Ni}(\text{CO})_4}^* = P_{\text{CO}}^4 / K^* \quad (2)$$

$$(P_{\text{CO}}^* = P_{\text{CO}})$$

Terms marked with asterisks represent equilibrium values. In contrast to this maximum possible or equilibrium partial pressure of carbonyl, the maximum available partial pressure is either the actual carbonyl pressure or the fictitious partial pressure that would result if all available carbonyl could remain stable under experimental conditions.

The stability index is the logarithm of the ratio of these two partial pressures.

$$\text{Stability index} = \log \frac{\text{maximum possible carbonyl pressure}}{\text{maximum available carbonyl pressure}} = \log \frac{P_{\text{Ni}(\text{CO})_4}^*}{P_{\text{Ni}(\text{CO})_4}}$$

Substituting the equilibrium relations in Equation 2 gives

$$\text{Stability index} = \log (P_{\text{CO}}^4 / P_{\text{Ni}(\text{CO})_4}) / K^*$$

Because the pressure ratio in this equa-

tion has an algebraic form similar to that of the equilibrium constant, it can be conveniently denoted by K without an asterisk.

$$\text{Stability index} = \log K / K^* \\ (P_{\text{CO}}^4 / P_{\text{Ni}(\text{CO})_4} = K)$$

The stability index can thus be computed from the ratio of two K values, one based on actual or fictitious pressures, the second on behavior at equilibrium. The stability index is positive when nickel carbonyl is stable, zero when it is in equilibrium with a trace of metallic nickel, and negative when it is unstable or more than trace amounts of metallic nickel are present.

The values for the equilibrium constant, K^* , required in these calculations were taken from Figure 2. Open circles represent determinations made in this laboratory; solid circles were computed from measurements made by Mittasch (8). Ideal gas behavior is assumed because it explains reaction behavior and dependable laws are not available for combining fugacities in mixtures as dense and complex as these.

Each curve in Figure 3 describes the behavior of a specified feed mixture at constant pressure and nearly constant residence time. The different values of the index along any curve arise from experiments at different temperatures. On the right, where the index is negative, conversions are low and the reaction consistently produces ionic or solid nickel. On the left, the index is positive and the catalyst is stable, but conversions are again low. However, conversions increase steadily as the stability index approaches zero from either side.

These curves lead to the conclusion that catalyst activity is highest when nickel carbonyl is in a condition of marginal stability. The data are not sufficient to develop either an analytical expression for activity or a definite

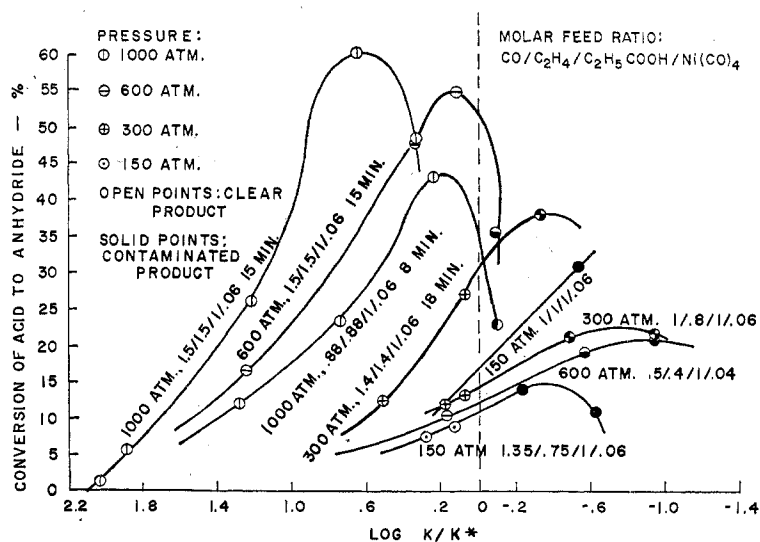


Figure 3. Effect of nickel carbonyl stability index on conversion of acid to anhydride and on character of product

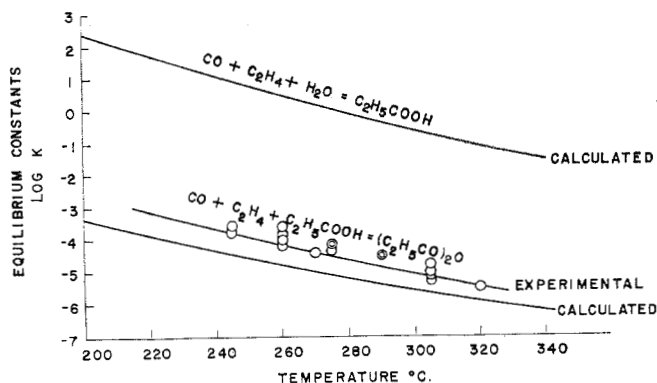


Figure 4. Effect of temperature on equilibrium constants

concept of reaction mechanism. However, Mittasch (8) and others (7-3, 9) have found evidence that nickel tetracarbonyl decomposes to a tricarbononyl that has not been isolated. If these two carbonyls can exist in dynamic equilibrium with each other, the concentration of the tricarbononyl should reach a maximum when the tetracarbonyl is barely stable. Hence, the tricarbononyl may be responsible for an important part of the maximum in activity.

If catalyst activity varies in this way with stability, it must also vary as the anhydride reaction consumes carbon monoxide. To study this, the equilibrium constants for the synthesis of propionic acid and propionic anhydride were estimated by standard thermodynamic techniques (Figure 4). The uncertainties, including those introduced by the assumption of ideal gas behavior, are equivalent to a temperature uncertainty of about 25° C.

These equilibrium constants were then used to estimate conversions at equilibrium. The results for one feed mixture used in anhydride synthesis are shown by

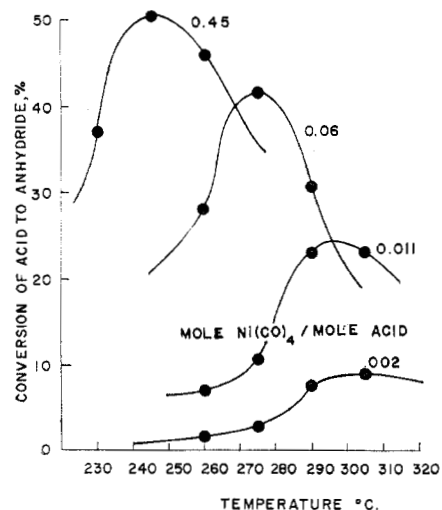


Figure 6. Effect of nickel carbonyl concentration on conversion of propionic acid to anhydride
Molar feed ratio 0.68 CO/0.68 C₂H₄/C₂H₅COOH

curves A (Figure 5). For each pressure there is a separate curve, showing that equilibrium conversion decreases as temperature is increased. At constant temperature equilibrium conversion increases as pressure is increased.

The isobars marked L show conditions for which the carbonyl stability index is zero and catalyst activity is highest. For each pressure carbonyl is stable and inactive to the left of the isobar, unstable and inactive to the right. As carbon monoxide is consumed by the anhydride reaction, the carbonyl becomes less stable and the carbonyl curve moves toward the left to lower temperatures.

Comparison of these carbonyl and anhydride curves for a single pressure—for example, 600 atm.—shows how actual conversions are restricted under different experimental conditions. For normal residence times of 10 to 20 minutes the optimum temperature is near that marked by the intersection of the carbonyl and anhydride curves. If operating temperature is greater than this value, the carbonyl decomposes and conversion is limited either by catalyst inactivity or by the relatively low values for conversion at equilibrium. If operating temperature is below that of the intersection, the carbonyl is stable but so inactive that conversions are limited to

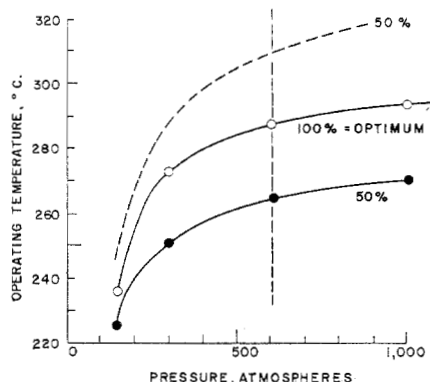


Figure 7. Effect of pressure on conversion of propionic acid to anhydride
Molar feed ratio 1.5 CO/1.5 C₂H₄/C₂H₅COOH/0.06 Ni(CO)₄

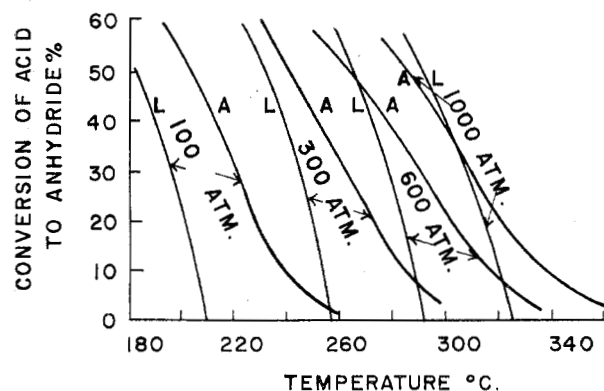


Figure 5. Calculated effect of temperature and pressure on conversion of propionic acid to anhydride

Molar feed ratio CO/C₂H₄/C₂H₅COOH/0.06 Ni(CO)₄.

small fractions of the equilibrium values. The optimum temperature should decrease slightly as residence time is increased. The optimum conversion appears to be slightly less than the equilibrium conversion expected for the optimum temperature.

Changes in composition at constant pressure produce shifts in these equilibrium curves and in the corresponding experimental curves. For example, an increase in carbon monoxide concentration makes the carbonyl more stable and increases the equilibrium conversion to anhydride. This shifts both curves to the right and increases the optimum temperature (Figure 1).

Increases in pressure also shift both the carbonyl and anhydride curves in Figure 5 to the right and increase optimum temperature. Because pressure enters the carbonyl calculations as its fourth power and the anhydride calculations as its square, the carbonyl curve moves more rapidly and overtakes the anhydride curve. This should pro-

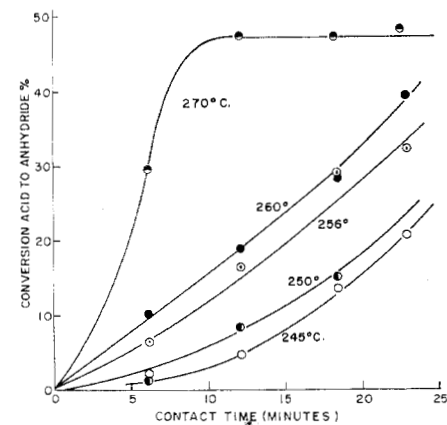


Figure 8. Effect of residence time on conversion of propionic acid to anhydride
Molar feed ratio CO/C₂H₄/C₂H₅COOH/0.06 Ni(CO)₄
Pressure 600 atm.

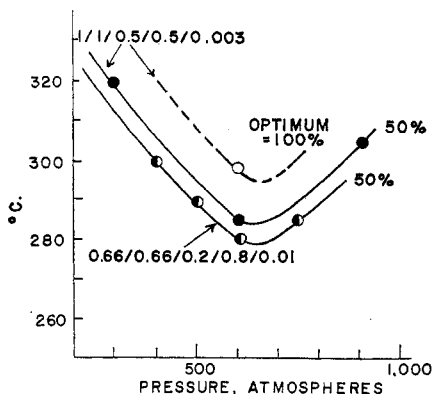


Figure 9. Effect of pressure on operating temperatures in synthesis of acid-anhydride mixtures

Complex fractions denote molar feed ratios $\text{CO}/\text{C}_2\text{H}_4/\text{C}_2\text{H}_5\text{COOH}/\text{H}_2\text{O}/\text{Ni}$

duce a decrease in optimum conversion at very high pressures.

The experimental curves in Figure 6 show the effects of increasing catalyst concentration. The location of the equilibrium isobar for anhydride in Figure 5 is almost unaffected by these changes in catalyst concentration, but the carbonyl isobar shifts to the left to lower temperatures as concentration increases and as stability decreases. This produces a sharp drop in the optimum temperature and a sharp increase in the optimum conversion.

The central curve in Figure 7 shows experimental values for the relation between optimum temperature and pressure. The lowest curve shows where high carbonyl stability and low catalyst activity have restricted conversions to half the optimum values. The highest curve (only a few data available) shows approximately where excessive temperatures result in half-optimum conversions. The limit is imposed by reduced activity or relatively low equilibrium conversions. An isobaric cross plot of these curves—for example, along the dotted line at 600 atm.—shows conversion against temperature similar to curves in Figures 1 and 6. Optimum conversions corresponding to points along the central curve increase steadily from 30% at 200 atm. to nearly 60% at 1000 atm. Because of limitations of the silver liner, these conversions could not be followed to the decreased values predicted by equilibrium curves for higher pressures and temperatures.

The effect on conversion of time in the converter is shown in Figure 8. Conversions for different residence times were determined by sampling the reaction mixture at a series of points along the converter. At 270° C. the conversion levels off sharply at 48% after about 10 minutes. This conversion can be assumed to be the equilibrium conversion for these conditions. Near the origin, the slopes of these curves increase with time. This appears to be a consequence of the in-

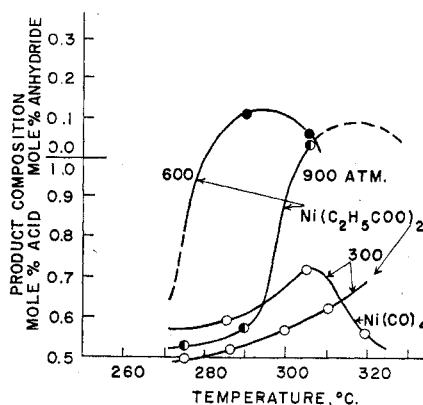
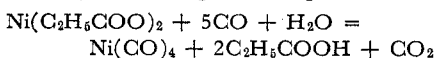


Figure 10. Effect of temperature and pressure on concentrations of propionic acid and anhydride in product

Molar feed ratio $\text{CO}/\text{C}_2\text{H}_4/0.5 \text{ C}_2\text{H}_5\text{COOH}/0.5 \text{ H}_2\text{O}/0.003 \text{ Ni}$

crease in catalyst activity that accompanies carbon monoxide consumption and decreasing catalyst stability.

The thermodynamic estimates indicate that propionic acid can be synthesized in high conversions under conditions similar to those used for anhydride synthesis. As water can be handled more easily and more economically than propionic acid, tests were run to determine whether part or all of the acid used in the feed could be replaced with water. It was expected that water would react in the converter with ethylene and carbon monoxide to generate acid needed for anhydride synthesis. Use of an aqueous feed allowed tests of dissolved nickel propionate as a catalyst precursor. It was expected that the propionate would be converted to carbonyl according to the equation



As shown in Figure 9, these changes in feed composition result in a minimum in the relation between optimum temperature and pressure. The minimum appears to be caused by relatively low conversion of nickel propionate to nickel carbonyl in the low-pressure region. In other respects, the behavior of the system is generally similar to that found with anhydrous feeds. Changes in feed composition shift curves like these downward if they bring the catalyst closer to marginal stability and upward if they make the catalyst more stable. Catalyst concentrations in these tests are so low that catalyst recovery is not economically necessary.

The corresponding isobars are shown in Figure 10. The two curves for 300 atm. imply that direct addition of nickel carbonyl produces higher conversions than with nickel propionate. This indicates that a substantial portion of the propionate is not converted to carbonyl under these conditions. At 600 atm. and below about 280° C. the reaction produces only propionic acid. At higher temperatures anhydride concentration

increases from 0 to about 10 mole % of the liquid product.

Consequently, feed compositions and operating conditions can be chosen so that this system of reactions will produce acid and anhydride in any desired ratio. At one extreme, product from the aqueous system can be restricted to acid; at the other, anhydrous feed yields anhydride only.

Conclusions

Nickel carbonyl is an effective catalyst for the synthesis of propionic anhydride from ethylene, carbon monoxide, and propionic acid and of propionic acid from ethylene, carbon monoxide, and water. At 300 to 600 atm., at 270° to 290° C., and with feed compositions that bring the nickel carbonyl catalyst to a state of marginal stability in the gases leaving the converter, 40 to 70% of the ethylene can be converted at yields of 94 to 98%. Conditions can be selected to produce mixtures of anhydride and acid in any desired ratio. When aqueous feed is used for acid synthesis, nickel propionate can be used as a catalyst precursor.

Acknowledgment

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Equipment Used

- (1E) Autoclave Engineers, Inc., Erie, Pa. Compressor for CO and mixtures of CO and ethylene: Hofer five-stage, type 5; capacity 10 cu. meters (STP) per hour; 1000 atm. max. delivery pressure.
- (2E) *Ibid.*, pump for liquid ethylene: Hofer booster compressor; capacity approx. 2.1 pounds ethylene per hour; 1000 atm. max. delivery pressure.
- (3E) *Ibid.*, for acid feed, pump for liquid ethylene specially equipped with stainless steel liner.
- (4E) Ingersoll-Rand Co., New York, N. Y., compressor for ethylene: three-stage, model ER-3; capacity 600 cu. feet (STP) per hour; 2500 lb. per sq. inch max. delivery pressure.

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