

PRODUCTION OF HYDROGEN VIA CATALYTIC
DECOMPOSITION OF AQUEOUS ALKALI FORMATES

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Introduction

Yoneda, et al, ^(1,2) have published in the 1940's a series of studies on the use of aqueous potassium carbonate solutions as high-pressure water gas shift catalysts. They showed that the initial step consisted of the reaction of CO with K_2CO_3 to produce KOOCH as follows:



and that this reaction was relatively rapid at temperatures of the order of 250-300°C. The second step, the decomposition of KOOCH to produce hydrogen by reaction (2) below, was shown to be relatively slow, however, in the above temperature range.



The use of catalysts to accelerate the water gas shift and presumably reaction (2) was also studied.^(1b) A number of metal carbonates were studied wherein those of Cd, Al, Zn, Cr, Sn and Co were most effective.

The combination of reactions (1a) and (2) with the decomposition of $KHCO_3$ via reaction (3) below,



is equivalent to the water gas shift, reaction, i.e.,



Somewhat later Royen and Erhard⁽³⁾ made a similar study of a nonaqueous water gas shift catalyst which consisted of K_2CO_3 impregnated on activated carbon. They showed that the mechanism followed the same route outlined by Yoneda, et al for the aqueous system.

The reactions in the "dry" charcoal supported system proceeded under much milder conditions than in the aqueous system because of the higher surface area of the charcoal absorbent and because the charcoal apparently possesses some catalytic activity for decomposition of KOOCH.

Neither set of investigators discussed the possibilities of a cyclic system wherein the CO absorption step is separated from hydrogen generation via formate decomposition.

It is the purpose of this paper to describe in summary form the work carried out sporadically in the CCDC laboratories over a period of years to evaluate the potential of such a cyclic system.

There are a number of alternatives in the way that such a system can be conducted but considerations given here are limited to the use of aqueous potash solutions wherein the CO absorption step is carried out noncatalytically while the formate

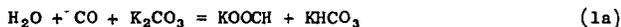
decomposition is conducted with the aid of a supported catalyst which has substantially no solubility in the aqueous reagent.

The system under consideration and experimental work to test its feasibility is described in what follows. Economic evaluation of the system is now underway at the CCDC laboratories, but no data on this question are available for presentation at this time.

Process Description

The system under consideration for removal of CO from a CO-rich gas and its conversion to a separate stream of hydrogen is illustrated schematically in Figure 1.

Formate synthesis is via noncatalyzed reactions (1a and 1b):



No distinction has been made in the discussion that follows between the rate of the two reactions. No experimental data to prove this equivalence are available, however.

The rationalization here is that the mechanism involves, as proposed by Royen and Erhard,⁽³⁾ the reaction of CO with hydroxyl ion. As long as the hydroxyl ion concentration is high enough to sustain mass transfer rate control, then the rate should be reasonably independent of the salt composition.

Various type of contacting devices for reactions (1a and 1b) have been investigated in a preliminary fashion as will be discussed below. A suitable device would be a gas sparged bubble column possibly packed with a catalytic inert packing to increase the gas-liquid interfacial area and accordingly the mass transfer rate. Suitable operating conditions will be discussed after the experimental data are presented.

It is essential to success of the system presented here that the formate synthesis via reactions (1a and 1b) proceed with a rate many fold greater than its noncatalytic decomposition via reaction (2). It will be shown below that this condition is readily achieved in practice.

The second essential step is the catalyzed decomposition of formate via reaction (2). The preferred system here is a fixed-bed catalyst, trickle-phase operation wherein steam is passed countercurrent to the descending stream of aqueous formate. The experimental system discussed, however, used a cocurrent system but this was done only for experimental convenience.

The gas leaving the formate decomposition will contain appreciable amounts of carbon dioxide and may contain in addition small but appreciable amounts of carbon monoxide. These must be removed from the final gas by conducting reactions (1a, 1b and the reverse of reaction 3). The reversal is effected by first partially decomposing the KHCO_3 in the effluent, liquid stream from the formate decomposition via steam stripping at a reduced pressure.

The K_2CO_3 enriched liquid is then used to absorb residual CO_2 and CO from the hydrogen-rich gas in a countercurrent column at a reduced temperature as shown.

Various types of CO-rich gas may be treated by the proposed process, but the discussion here is limited to treatment of a low hydrogen and methane content gas. A generic schematic system for generation of a CO-rich gas integrated with the formate system is shown in Figure 2.

The system shown in Figure 2 envisions generation of a low hydrogen and methane content gas via gasification of a hydrogen deficient fuel such as coal or char. A particularly suitable feedstock, for example, is a low temperature char produced by fluid bed carbonization of the residue from coal extraction or hydroextraction.

The hydrogen and methane contents are maintained low by operating at a relatively high exit temperature from the gasifier, i.e., at 1750°F or above, and by recycle of CO₂ to the gasifier rather than by use of steam.

The CO₂ is supplied either by recycle of the tail gas from the formate system or by CO₂ evolved from the KHCO₃ decomposition or both as illustrated in Figure 2.

The gasifier itself may be operated with air, oxygen-enriched air or relatively pure oxygen depending in part on the specific type of gasifier chosen. Various types of gasifiers may be used here including entrained phase, fluid bed or fixed bed systems but it is outside the scope of this paper to discuss the gasification step further.

The system shown in Figures 1 and 2 makes no special provision for removal of sulfur from the gas. When the system is applied to relatively low-sulfur subbituminous coals or lignites, the major fraction of the sulfur will be retained in the coal ash, at least when a fluid bed gasifier is used. A considerable amount of sulfur will also be rejected with the CO₂ in the KHCO₃ decomposition steps. The result should be that the residual gas would be low enough in sulfur after incineration for direct release to the atmosphere.

Experimental

The experimental procedure used in the course of this work will only be described in summary form because of the large number of different topics covered.

The noncatalytic synthesis of formate by reaction of CO with aqueous carbonate was studied by a number of different methods. A continuous reactor system using a 3" ID x 9" pool height, stirred reactor was previously described.⁽⁴⁾ Kinetic studies were likewise made using the same reactor operated batchwise with respect to the liquid but continuously with respect to the gas. Continuous studies were also made in a stirred pilot plant reactor. The reaction system and its operation was identical to that previously described in connection with its use for the analogous noncatalyzed reduction of K₂S₂O₃.⁽⁵⁾ with CO. The reaction was also studied in a 3" ID continuous gas-sparged bubble column.

The catalytic decomposition of aqueous formate was studied in both batch and continuous equipment. The batch apparatus used the same 3" ID stirred reactor employed for formate synthesis.⁽⁴⁾ The apparatus was used initially for screening studies of various metals and metal sulfides supported on activated carbon. Finally, the apparatus was used for equilibrium studies in the decomposition of formate via reaction (2). The best catalyst found from the screening study, i.e., 9% Mo as MoS₂ on 12 x 20 mesh Darco activated carbon, was used in this work. The apparatus was modified to permit sampling of both the gas and liquid phase at various times to determine steam partial pressures over the liquid phase. A pressure of 35-40 atmospheres of carbon dioxide was impressed on the system to eliminate complications due to decomposition of potassium bicarbonate. Equilibrium was assured in reaction (3) by approaching it from both sides, i.e., via synthesis as well as decomposition of formate.

The continuous unit studies of the decomposition of aqueous formate were conducted using a fixed-bed, trickle phase system. The same 12 x 20 mesh MoS₂ on carbon catalyst used in the equilibrium studies was also used in this work. The 1-1/4" ID reactor was constructed of Hastelloy C to eliminate stress corrosion. It was operated cocurrently

with respect to liquid feed and gas withdrawal. A schematic sketch of the equipment used is shown in Figure 3. The liquid feed was distributed evenly over the catalyst bed by means of a cup with holes in the perimeter. The catalyst bed was 26" high. The lower 22-1/4" of the reactor was packed initially with Cannon stainless steel packing. This was later replaced, because of corrosion, with the same height of mullite beads. The inert packing was operated at a temperature between 55 and 90°F below the catalyst section in order to partially reabsorb any carbon dioxide evolved via reaction (3). A three hour line-out period was universally used before initiation of the material balance operation to obtain the data reported here.

The catalyst was prepared by impregnation of the activated carbon with aqueous ammonium molybdate. The catalysts were dried and calcined in a nitrogen stream at 550°F for four hours, followed by sulfiding for four hours at 550°F with 15 mol % hydrogen sulfide in hydrogen.

Gas analyses were conducted by standard gas chromatography.

The liquid samples were analyzed for potassium formate via use of excess potassium permanganate as an oxidant followed by back titration with ferrous ammonium sulfate.

The bicarbonate content was determined by use of excess KOH to convert it to carbonate. The carbonate was converted to unreactive form by precipitation with barium chloride and the excess KOH determined by titration with HCl.

Total carbonate plus sulfide sulfur were determined by acidifying the sample with dilute sulfuric acid and removal of the H₂S and CO₂ by purging with nitrogen. Hydrogen sulfide was recovered and analyzed iodimetrically. Carbon dioxide was determined gravimetrically by absorption on Ascarite after drying the gas with magnesium perchlorate.

Rate of Formate Synthesis

The rate of formate synthesis via reactions (1a and 1b) was studied in a number of different types of experimental units as outlined above. The most extensive study was made in the 3' ID continuous stirred unit. A summary of results obtained in this study was presented previously.⁽⁴⁾

It is outside the scope of this paper to give detailed results of the formate synthesis. Only summarized conclusions will be presented.

The reaction at temperatures above 400°F has the characteristics of a liquid film mass transfer controlled process.⁽⁶⁾ The reaction rate has a low temperature coefficient of the order of 10 Kcal/mol of CO absorbed, the rate is first order with respect to CO pressure and increases at least linearly with agitator speed. The absolute formate synthesis rate is approximately equivalent to the rate of CO consumption in the noncatalyzed reduction of aqueous thiosulfate which were reported earlier.⁽⁵⁾

It also has been found more recently that the formate synthesis rate, like the thiosulfate reduction rate,⁽⁵⁾ increases markedly with decreasing salt concentration down to at least about 35 wt % salt concentration. The effect of salt concentration is probably related to the decreasing solubility of CO with increasing salt concentration⁽⁷⁾ which in turn would have the effect of decreasing the mass transfer rate, R, of CO, i.e.,

$$R = k_v \alpha P_{CO} \quad (5)$$

The reaction rate undergoes a transition to a chemical reaction rate controlled regime as the temperature is reduced to 400°F and below. The rate apparently is negligibly slow under conditions where the hot potassium carbonate process for removal of acid gases normally operates, i.e., at ca 200-240°F.

The reaction rates previously reported⁽⁴⁾ were relatively low. The specific rate at 482°F, for example, was 7×10^{-3} lb mols/hr-ft³-atm. One reason for the low rate was the high salt concentrations, i.e., 70 wt % employed. More recent data have shown specific rates at 450°F as high as 2×10^{-1} lb mols/hr-ft³-atm using more dilute, i.e., 35 wt %, salt solutions.

The above specific rates are based on unit volume of the aerated liquid, not as is often done, to base the rates on unit volume of unaerated liquid.

The commercial embodiment would preferably use a nonmechanically agitated contactor. A gas-sparged bubble column contactor (BCC) would be suitable for this purpose. Many investigators^(8,9) have studied mass transfer processes in BCC reactors. The rate is approximately proportional to the seven-tenths power⁽¹⁰⁾ of the superficial gas velocity (V_g). At highly turbulent conditions, i.e., $V_g \approx 0.7$ ft/sec, the rate in a BCC reactor⁽⁸⁾ approaches that of a vigorously mechanically stirred reactor.

The BCC has another advantage over a mechanically agitated reactor in that the gas flow pattern approaches piston flow.

A few experiments were carried out in the CCDC laboratories in a 3" ID BCC reactor but much more remains to be done. The preliminary data confirm expectations from the literature that high rates can be obtained in a BCC reactor.

Rate of Formate Decomposition

Formate decomposition via reaction (2) must obviously be minimized during synthesis via the noncatalyzed reaction with CO. The decomposition of formate is quite slow in the absence of a catalyst such that normally this is not a problem. Metal surfaces are usually readily poisoned for this reaction by treatment with hydrogen sulfide.

Conversion of CO to hydrogen was only of the order of one mol percent, for example, in the pilot plant stirred reactor operated at 540°F, 720 psig and 35 minutes residence time. Under the above conditions 88 mol % conversion of carbonate to formate was achieved.

Equilibrium Data

There are five equilibria which completely define the system as long as the only species present in the liquid phase are KOOCH, KHCO₃, K₂CO₃ and H₂O, and the only species in the gas phase are CO, CO₂, H₂ and H₂O. The appropriate equilibria are the steam pressure over the salt solutions, equilibria in reactions (2, 3 and 4), respectively, and salt solubility relationships.

Steam Pressure

The steam equilibrium pressure decreases with increasing salt concentration. It is desirable, of course, to operate with as low a steam pressure as possible. It is not, however, entirely practical to do this by indefinitely increasing the salt

concentration. The use of more concentrated salt solutions incurs the disadvantages of decreased reaction rate, limited solubility of one of the components - usually KHCO_3 , and increased viscosity.

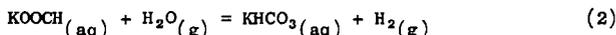
The steam partial pressure in the $\text{KOOCH-K}_2\text{CO}_3\text{-KHCO}_3\text{-H}_2\text{O}$ system was correlated against the parameter of mols K/1000 gm H_2O . The basic assumption here is that all salt solutions in the above system have the same vapor pressure at the same value of the above parameter. Insufficient experimental data were obtained to verify this assumption precisely. It is useful, however, as a means of roughly predicting the vapor pressure of steam over a given salt solution.

Experimental data are presented in Figure 4 for three series of salt solutions as a function of temperature on a semi-log plot of vapor pressure versus the reciprocal of the absolute temperature. The lines correspond to the least squares regression through the experimental points. The heats of vaporization calculated from the regression lines are reasonably close to that of pure water at this temperature, namely, 9.0-9.3 Kcal/mol.

Figure 5, is a cross plot of the data of Figure 4 with temperature as parameter.

Equilibrium in Formate Decomposition

The equilibrium in reaction (2),



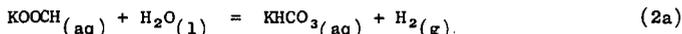
was studied using solutions equivalent to 40 wt % KOOCH or 9 mols K/1000 gm H_2O . Equilibrium was approached from both directions by use of the MoS_2 catalyst.

The "equilibrium constant" in the above reaction, i.e.,

$$K = \frac{(\text{KHCO}_3) P_{\text{H}_2}}{(\text{KOOCH}) P_{\text{H}_2\text{O}}}$$

is not independent of the concentrations and partial pressure ratios due to the large deviation from ideality, particularly of the salt components. Accordingly, the "equilibrium constant" of reaction (2) is plotted as a function of the molar ratio $(\text{KHCO}_3)/(\text{KOOCH})$ in Figure 6. Regression analysis was again used to locate the "best" straight lines to represent the data.

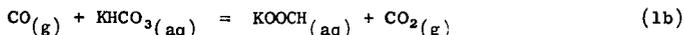
Figure 7 shows the partial pressure of hydrogen as a function of the fraction of KOOCH decomposed via reaction (2) with temperature as a parameter. It is immediately apparent that the hydrogen partial pressure is almost independent of temperature. Thus, if equilibrium in reaction (2) is expressed in the form,



it is immediately obvious that the heat of reaction (2a) is substantially zero.

Equilibrium in Formate Synthesis

Equilibrium in the formate synthesis reaction (1b),



may be expressed simply as the sum of the reverse of reaction (2) and the water-gas shift reaction (4), and accordingly,

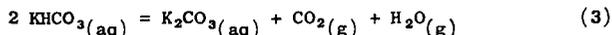
$$K_{1b} = K_4/K_2$$

The measured and equilibrium values for the water-gas shift ratio and the calculated equilibrium ratio PCO_2/PCO for reaction (1b) at a molar ratio of $KHCO_3/KOOCH = 1$, are given in Table I. It is immediately clear that the equilibrium in reaction (1) is highly favorable and there is little equilibrium limitation to prevent nearly complete absorption of CO .

The experimental values for the water-gas shift ratio obtained in the equilibrium study of reaction (2) were usually somewhat higher than equilibrium. This indicates that equilibrium was not quite achieved in the reverse of reaction (1b).

Equilibrium in Bicarbonate Decomposition

The equilibrium in reaction (3), i.e.,



is now needed for definition of the system. Unfortunately, the system described here operates at higher temperatures and higher salt concentrations than is usually employed in the "hot pot" process. The equilibrium relationships are further complicated by the presence of $KOOCH$. Thus, the data previously presented for reaction (3), in connection with the "hot pot" process by Tosh, et al.⁽¹¹⁾ and by Bocard and Mayland⁽¹²⁾ are of little value for the present case.

A limited equilibrium study for reaction (3) was, however, made in the course of the development of the CCDC Stack Gas Scrubbing Process⁽⁵⁾ in the $KHS-KHCO_3-KOOCH-H_2O$ system. The data have somewhat limited applicability to the present case because of the presence of KHS . Some data in the range of interest to the present process are shown in the curves given in Figure 8.

These data are compared with the data on the actual system in Figure 8 for two sets of experiments. The first set was obtained in the continuous unit where the effluent from the catalytic bed was run over an inert bed of packing at the temperature indicated. Equilibrium, accordingly, was not necessarily approached. It is noted that the partial pressure of CO_2 in the continuous unit series appears significantly lower than the values expected from the equilibrium data.

A possible explanation is that the continuous unit data are low due to further absorption of CO_2 in the effluent lines and receivers. The receivers were operated at a temperature usually about $100^\circ F$ lower than the inert packed bed, but relatively poor contact between gas and liquid was provided. It is, nevertheless, to be expected that some additional CO_2 absorption occurred. It should be noted also that the equilibrium pressure of CO_2 should be somewhat lower in the continuous unit series because of the higher water and $KOOCH$ contents. It is clear from the equilibrium data, for example, that the addition of $KOOCH$ at the same water content suppresses the CO_2 dissociation pressure.

Data from a second set of experiments in the batch unit are also indicated on Figure 8. These data were obtained by cooling the batch autoclave from the decomposition temperature to $437^\circ F$ and holding at this lower temperature for 30 minutes. The deviation from the equilibrium CO_2 pressure should, in contrast to the continuous series, be on the high side in these runs.

The batch data are somewhat scattered as shown, but are in the approximate range expected from the equilibrium data.

It is obvious that more data are required to elucidate the equilibrium pressures in the actual system more closely.

Salt Solubility Relationships

It is outside the scope of this paper to present any data on the above subject. However, due to the higher temperature at which this system operates as compared with the "hot pot" system, no problem is incurred because of the presence of insoluble salts as long as the total salt concentration is below about 50 wt % and the temperature is maintained above about 250°F.

Rate Data on Catalytic Decomposition of KOOCH

A screening study of various metal sulfides supported on activated carbon was made in the batch autoclave as catalysts for reaction (2). The best catalysts found were the group VI sulfides typified by MoS₂ and the noble metals.

The continuous unit studies were limited therefore to the uses of MoS₂ and Pt catalysts. It soon became obvious that the MoS₂ catalyst was much more active than the Pt catalyst and accordingly only results from the former catalyst will be presented.

The feed solution and catalyst used in the continuous unit runs presented here were of constant composition as given in Table II.

The liquid hourly space velocity (LHSV) was varied between 2 to 4 at two operating temperatures, i.e., 425 and 475°F. One run was made at 525°F at a space velocity of 3. The liquid and gas product compositions for the two series are given in Tables III and IV, respectively. It is immediately noted that high purity hydrogen is generated in the range of 96.5 to 99.5 mol %. The major impurity is CO₂.

The product composition expressed as the fraction $(\text{KHCO}_3) / [(\text{KHCO}_3) + (\text{KOOCH})]$, equivalent to fractional decomposition of KOOCH via reaction (2), is plotted as a function of LHSV in Figure 9 where it is compared with the equilibrium values. The equilibrium values are estimated from the product gas and liquid compositions without any correction for changes that occur on cooling. The hydrogen partial pressure used to estimate the decomposition parameter is arrived at from the dry gas composition and the steam partial pressure obtained from Figures 4 and 5. It is noted that at 475°F, equilibrium is closely approached as the LHSV is reduced to a value of 2. The one run at 525°F showed a higher than equilibrium conversion which is obviously impossible. The product liquid and gas compositions were actually those measured after cooling to 435°F. Thus, the KHCO₃ content at the reaction temperature of 525°F was undoubtedly somewhat lower due to partial decomposition via reaction (3). The hydrogen partial pressure is also slightly lower at the higher temperature. These factors would cause the experimental decomposition ratio to shift downward and the calculated ratio to shift upward slightly. It would appear, in any case, that true equilibrium is closely approached at 525°F and LHSV = 3.

Catalyst Life

Studies not reported here with more concentrated salt solutions indicated a very short catalyst life. The major reason for the catalyst activity decline was traced to the deposition of insoluble salts, probably KHCO₃, blocking the catalyst pores. A major improvement in catalyst life was achieved by use of the more dilute solution shown in Table II.

The results of a prolonged run are given in Figure 10. It is noted that after a brief relatively rapid decline, that the activity decline with time is relatively slight. The experimental data on the rate of decline after 35 hours onstream was fitted by a linear regression equation:

$$y = 52.92 - 0.0075 t.$$

where y is the percent formate decomposed and t is the time in hours.

The above equation cannot realistically be used beyond the range of the data, i.e., 121 hours. It is obvious that longer runs are required to establish a realistic value for catalyst life.

Process Operating Conditions

Considerably more data are required to establish optimum operating conditions for the process than has been presented here.

It is clear, however, that the salt concentration should be below 60 wt %, because of the adverse effect of high salt concentration on the rate of formate synthesis, but probably above 35 wt %. The operating temperature in the formate synthesis reactor should be above 400°F, but preferably below 500°F to avoid excessive steam vapor pressures. A suitable temperature is approximately 450°F.

Approximate sizing of the formate synthesis reactors may be obtained by considering the simplest case where synthesis is via reaction (2), i.e., no change in gas volume occurs, and a BCC type reactor is used such that piston flow of gas may be assumed.

The appropriate rate equations in differential and integrated forms are:

$$-dF_{CO} = \frac{k_G \pi F_{CO} dV}{F} \quad (6)$$

$$2.303 \log \left(\frac{1}{1-\alpha} \right) = \frac{k_G \pi V}{F} \quad (7)$$

A hypothetical case was considered using equation (7) in a BCC reactor for production of 25,000 lb mols H_2 /hr from dry producer gas containing 35 mol % CO . The conditions used are illustrated in Table V. The basic assumption on reaction kinetics is that the maximum rate realized in a mechanically agitated contactor, i.e., $k_G = 0.2$ lb mols/hr-ft³-atm at 450°F can also be achieved in a BCC contactor at a superficial velocity of 0.75 ft/sec. This has not been demonstrated as yet and may very well prove to be optimistic. Obviously more experimental work is required. Under the conditions specified in Table V, three 12' diameter vessels with a liquid pool height of 50' would be required. To maintain the desired superficial gas velocity, the reactors would have to be operated in parallel.

It is clear from the data in Table V, that the minimum operating pressure for the formate synthesis reactor when operated with producer gas is of the order of 60 atm. The operating pressure may be reduced somewhat if the gasifier is operated with oxygen or oxygen-enriched air, but obviously must always substantially exceed the vapor pressure of the salt solution which at 450°F amounts to 24 atm.

The catalytic formate decomposition reactor should operate generally at temperatures somewhat higher, i.e., 25-100°F, than the synthesis reactor. Countercurrent flow of steam versus the formate solution will permit operation at maximum pressure with minimum steam consumption. The total operating pressure should be at least equal to that in the formate synthesis reactor. The data of Figure 7, for example, indicates that pressures as high as 100 atm are practical at 525°F in a countercurrent system.

The gas leaving the catalytic decomposition zone will contain appreciable amounts of carbon dioxide. This must be removed by scrubbing with the K_2CO_3 enriched reagent as discussed previously. The scrubbing temperature must be below 400°F, but desirably above 250°F to prevent deposition of insoluble salts.

Conclusions

The aqueous formate process for treating a CO-rich gas, with separation and conversion of the CO to a separate stream of pure hydrogen has been shown to be technically feasible. More experimental work is required to ascertain optimum operating conditions. The economic potential also remains to be determined.

The process is limited in scope to treatment of gases at relatively high pressure, i.e., above about 40 atmospheres.

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Nomenclature

k_G = mass transfer rate, lb mols/hr-ft³-atm.

k_V = volumetric mass transfer rate, hr⁻¹.

α = CO solubility, lb mols/ft³-atm.

P_{CO} , P_{H_2} , etc. = partial pressure of gas, atm.

(KOOCH), (KHCO₃), etc. = mols of salt in question/unit volume.

V = volume of aerated liquid, ft³.

π = total pressure, atm.

F_{CO} = carbon monoxide flow rate, ft³/hr.

F = total gas flow rate, ft³/hr.

α = fractional absorption of carbon monoxide.

References

1. Yoneda, K, Kondo, S., and Abe, R., Jour. Chem. Soc., Japan
 - a. 44, 385 (1941).
 - b. 44, 388 (1941).
 - c. 46, 667 (1943).
 - d. 47, 5 (1944).
 - e. 47, 7 (1944).
2. Yoneda, K., Honda, Y, Momiyama, N, and Abe, R., Jour. Chem. Soc., Japan 46, 554 (1943).
3. Royen, P., and Erhard, F.,
Erdol und Kohle 6, 195 (1953).
Ibid 9, 19 (1956).
4. Yavorsky, P.M., Mazzocco, N.J., Rutledge, G.D., and Gorin, Everett,
Environ. Science & Tech. 4, 757 (1970).
5. Struck, R.T., Gorin, Everett, and Clark, W.E.,
Paper presented at 68th AIChE Annual Meeting,
Los Angeles, Calif., Nov. 16-20, 1975.
6. Higbie, R., Trans. AIChE, 31, 365 (1935).
7. Wise, D.L., and Houghton, G., Chem. Eng. Science, 23, 1211 (1968).
8. Braulick, W.J., et al., AIChE, J. 11, 73 (1965).
9. Juvekar, V.A., and Sharma, M.M., Chem. Eng. Sci., 28, 825 (1973).
Ibid , 28, 977 (1973).
10. Mashelkar, R.A., Brit. Chem. Eng., 15, (10) 1297 (1970).
11. Tosh, J.S., et al., Bureau of Mines Reports of Investigations, 5484 (1959).
12. Bocard, J.P., and Mayland, B.J.,
Hydrocarbon Proc. & Pet. Ref., 41, 128 (1962).

TABLE I

Estimated Equilibria in Reaction 1b
 $\text{CO} + \text{KHCO}_3 = \text{KOOCH} + \text{CO}_2$

Temp., °F	Water-Gas-Shift Ratio,		Equilibrium Values at $(\text{KHCO}_3)/(\text{KOOCH}) = 1$	
	$\frac{P_{\text{CO}_2}}{P_{\text{H}_2}}$ Equilibrium	$\frac{P_{\text{H}_2}/P_{\text{H}_2\text{O}}}{P_{\text{CO}}}$ Expt'l Range	$\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$ (expt'l)	$\frac{P_{\text{CO}_2}}{P_{\text{CO}}}$ (calc'd)
425	141	150-280	1.7	83
475	87	88-101	0.92	95
525	56	53-74	0.64	88

TABLE II

Composition of Feed Solution and Catalyst in
Continuous Formate Decomposition Experiments

Solution

KOOCH	38.90 Wt %	$\frac{\text{Mols K}}{1000 \text{ gms H}_2\text{O}} = 12.45$
K ₂ CO ₃	10.60 Wt %	
KHS	0.45 Wt %	
H ₂ O	50.05 Wt %	$\frac{\text{Mols KOOCH}}{1000 \text{ gms H}_2\text{O}} = 9.25$

Catalyst

9% Mo as MoS₂ on 12 x 20 mesh Darco activated carbon.

TABLE III

Product Compositions in Continuous
Catalytic Decomposition of KOCH

Catalytic Decomposition Temp., °F CO ₂ Absorption Temp., °F	←————— 475 —————→			
	400	415	414	415
LHSV	3	3	2	4
<u>Liquid Product</u>				
<u>Mol Fraction of K as</u>				
KOCH	0.372	0.389	0.329	0.466
K ₂ CO ₃	0.278	0.284	0.285	0.231
KHCO ₃	0.350	0.327	0.386	0.303
Mol Fraction K ₂ CO ₃ Converted to KHCO ₃	0.558	0.535	0.577	0.567
<u>Dry Exit Gas, Mol %</u>				
H ₂	96.72	96.83	96.65	97.90
CO ₂	3.11	3.00	3.22	1.98
CO	0.13	0.13	0.11	0.11
H ₂ S	0.02	0.04	0.02	0.01
CH ₄	0.02	0.00	0.00	0.00
Total Pressure, atm	←————— 52.65 —————→			
Est. Partial Pressure H ₂ O at 475°F, atm	←————— 32 —————→			
Est. Partial Pressure H ₂ O at 415°F, atm	←————— 15.0 —————→			
Partial Pressure CO ₂ at 415°F, atm	1.17	1.13	1.21	0.75

TABLE IV

Product Compositions in Continuous
Catalytic Decomposition of KOOCH

Catalytic Decomposition Temp., °F	←----- 425 -----→		
CO ₂ Absorption Temp., °F	365	370	370
LHSV	3	2	4
<u>Liquid Product</u>			
<u>Mol Fraction of K as</u>			
KOOCH	0.576	0.613	0.657
K ₂ CO ₃	0.207	0.204	0.206
KHCO ₃	0.217	0.183	0.137
Mol Fraction K ₂ CO ₃ Converted to KHCO ₃	0.513	0.472	0.400
<u>Dry Exit Gas, Mol %</u>			
H ₂	98.88	99.21	99.58
CO ₂	1.05	0.75	0.39
CO	0.05	0.03	0.02
H ₂ S	0.02	0.01	0.01
CH ₄	0.00	0.00	0.01
Total Pressure, atm	←----- 44.5 -----→		
Est. Partial Pressure H ₂ O at 425°F, atm	←----- 17.6 -----→		
Est. Partial Pressure H ₂ O at 370°F, atm	←----- 9.2 -----→		
Partial Pressure CO ₂ at 370°F, atm	0.37	0.26	0.14

TABLE V

Sizing of Formate Synthesis Reactor

Operating Conditions for Production - 25,000 lb mols/hr H₂

Temperature	450°F	
Total Pressure	80 atm	
Salt Concentration	<u>10 mols K</u> 1000 gms H ₂ O	- equivalent to 46 wt % salts as KOOCH
Steam Partial Pressure	24 atm	
Mol Fraction CO in Dry Producer Gas	0.35	
CO Mass Transfer Rate	0.2 lb mols/hr-ft ³ -atm	
Percent Absorption CO	91.2	
Superficial Gas Velocity	0.76 ft/sec	
No. of 12' ID x 50' Vessels	3	

FIGURE 1
 HYDROGEN PRODUCTION FROM CO-RICH GAS
 VIA
 FORMATE SYSTEM

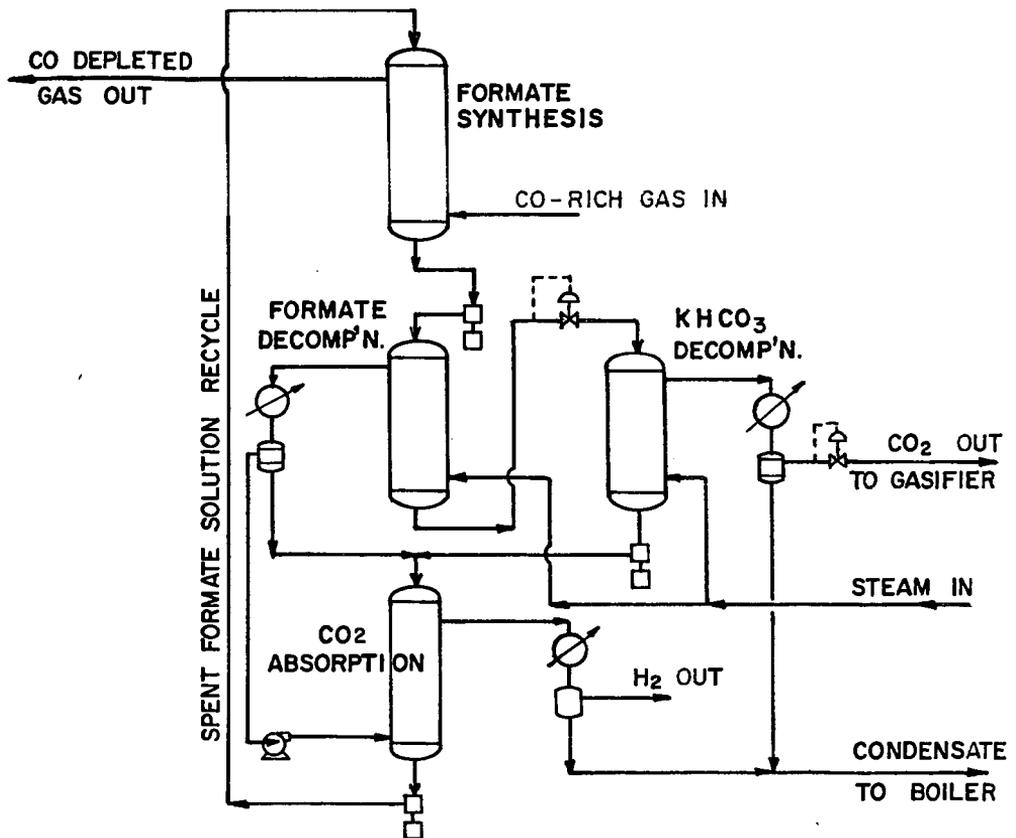


FIGURE 2
 GENERATION OF CO-RICH GAS
 SCHEMATIC SYSTEM

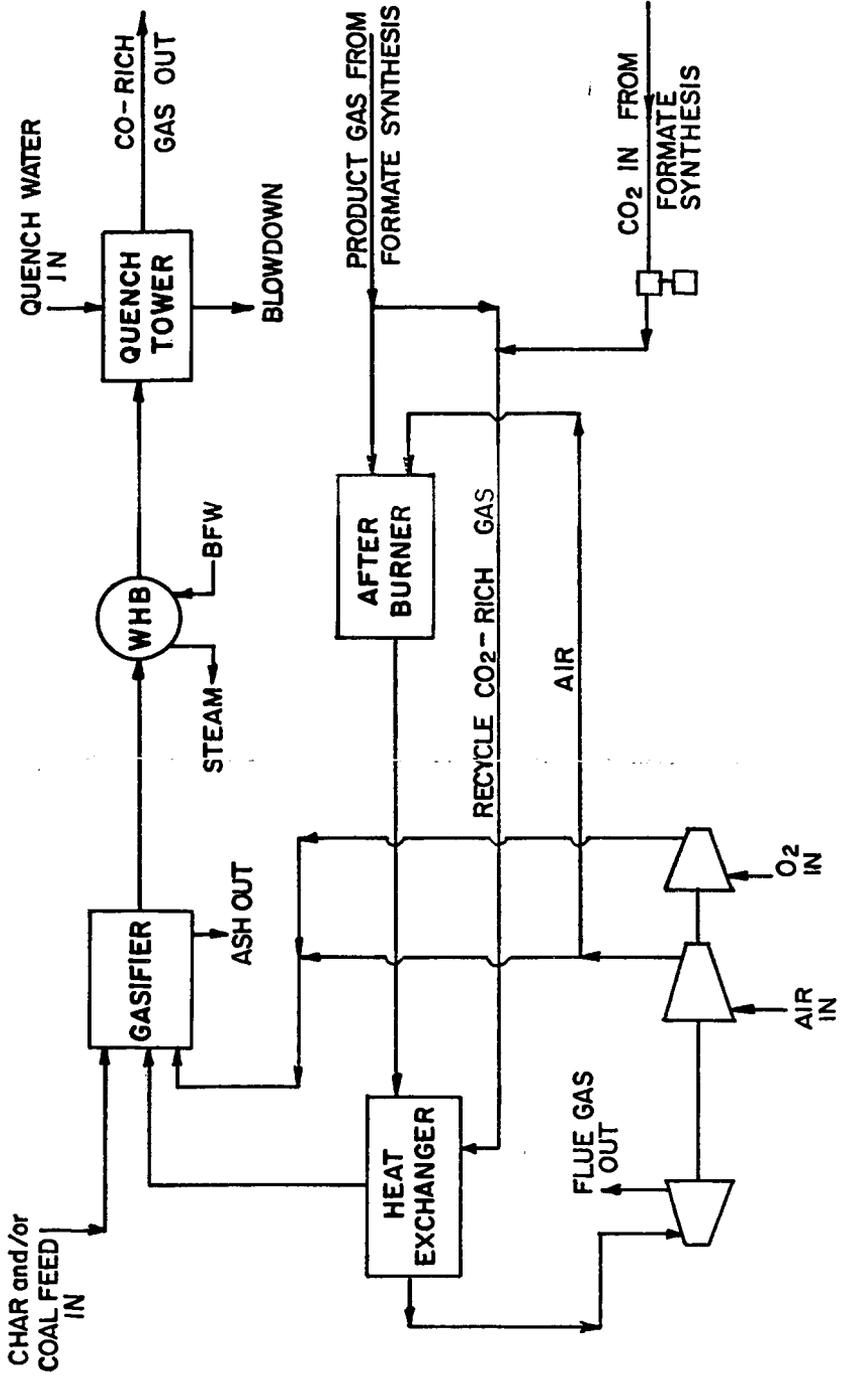


FIGURE 3

SIMPLIFIED SCHEMATIC FLOW SHEET
CONTINUOUS UNIT FOR CATALYTIC DECOMPOSITION
OF AQUEOUS FORMATE

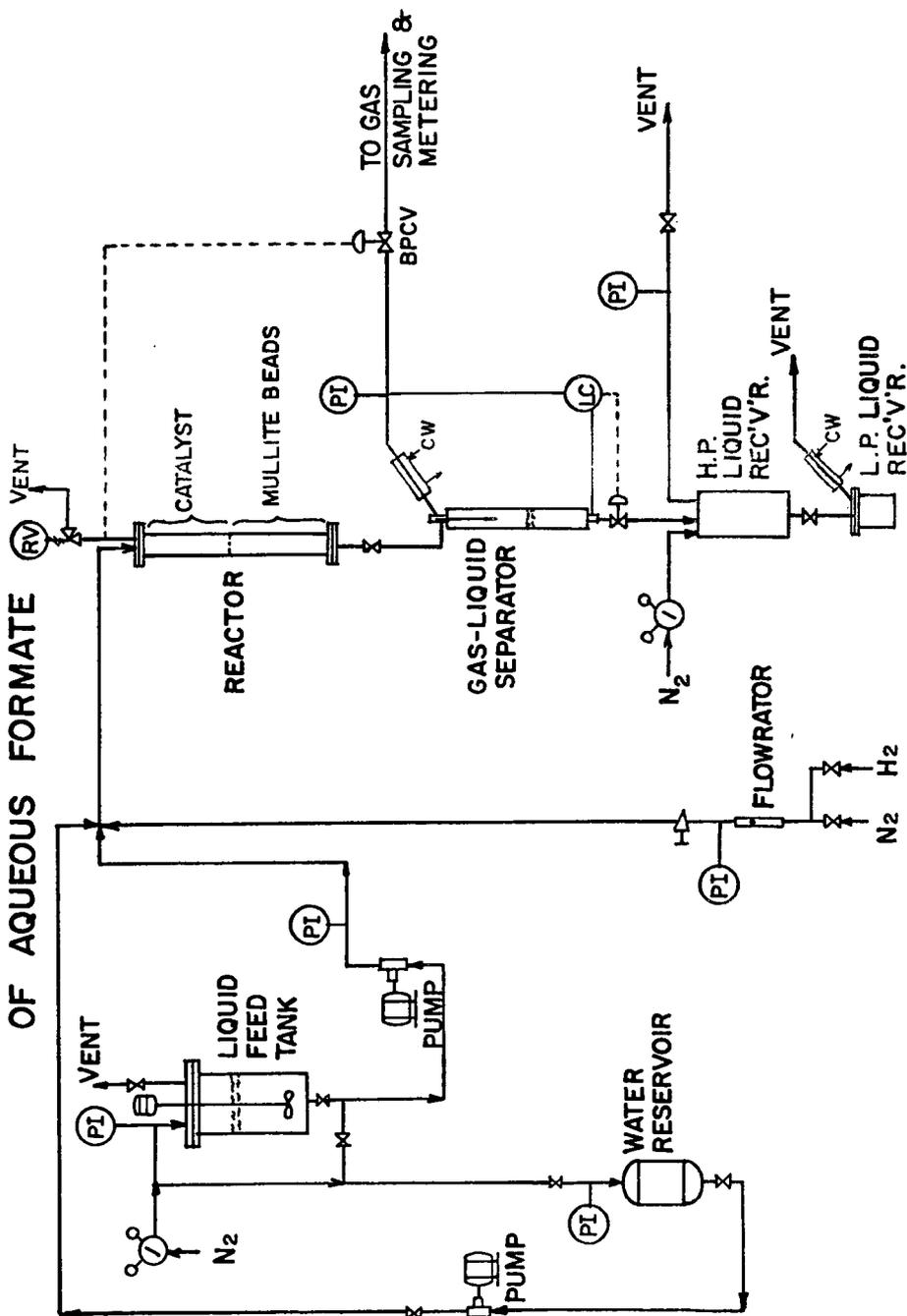


FIGURE 4

STEAM PARTIAL PRESSURE OVER
 $\text{KOOCH} - \text{K}_2\text{CO}_3 - \text{KHCO}_3 - \text{H}_2\text{O}$ SOLUTIONS

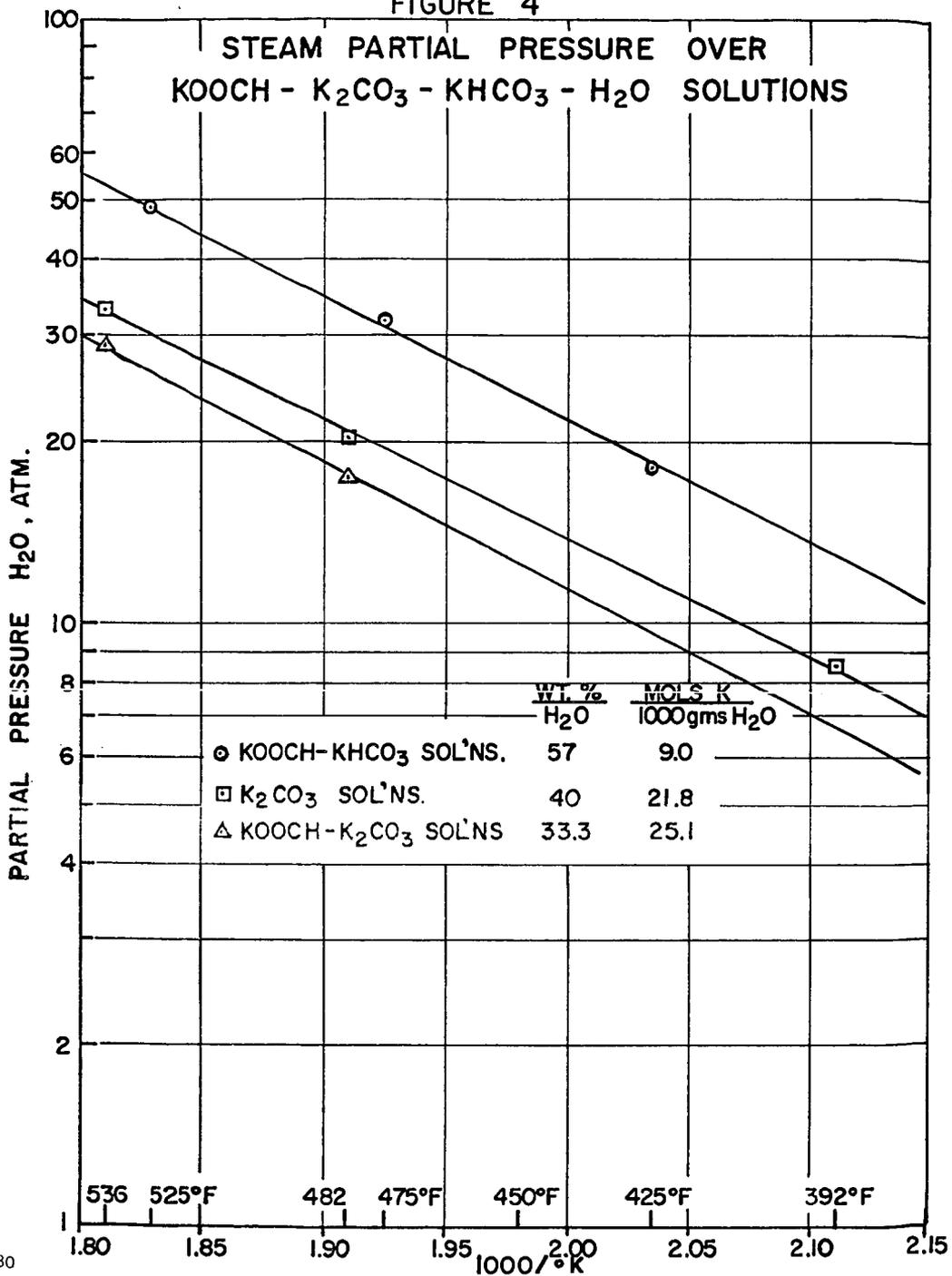


FIGURE 5
STEAM PARTIAL PRESSURE
vs SALT CONCENTRATION

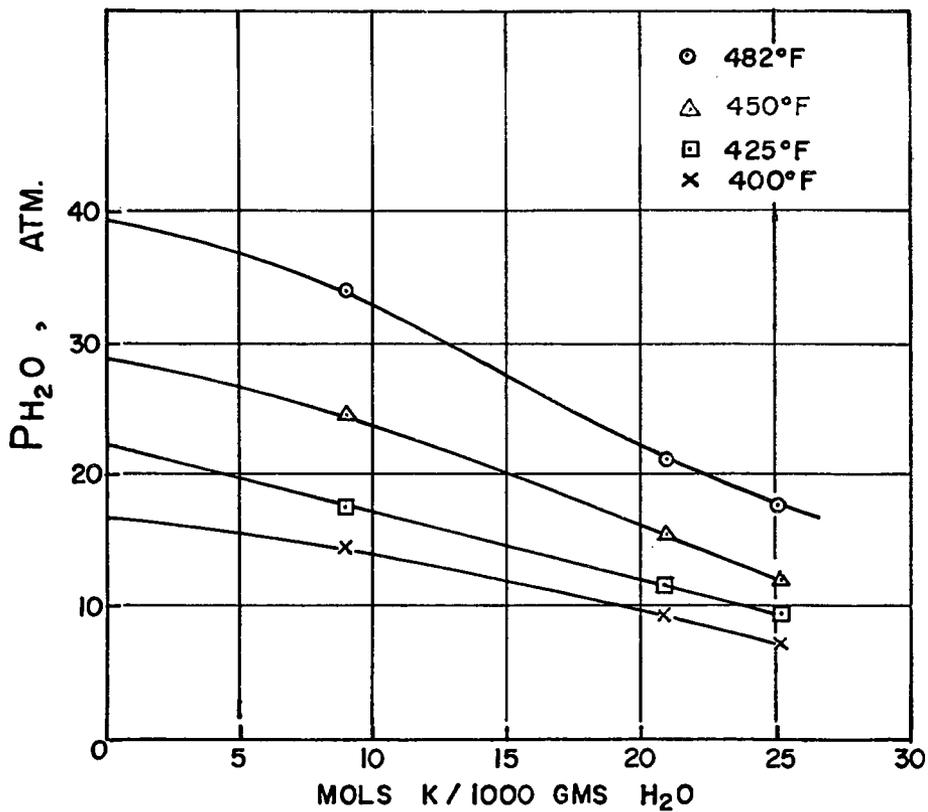


FIGURE 6
EQUILIBRIUM DATA
DECOMPOSITION AQUEOUS KOOCH

$$\frac{\text{Mols K}}{1000\text{gms H}_2\text{O}} = 9.0$$

$$\text{WT. \% H}_2\text{O} \cong 57$$

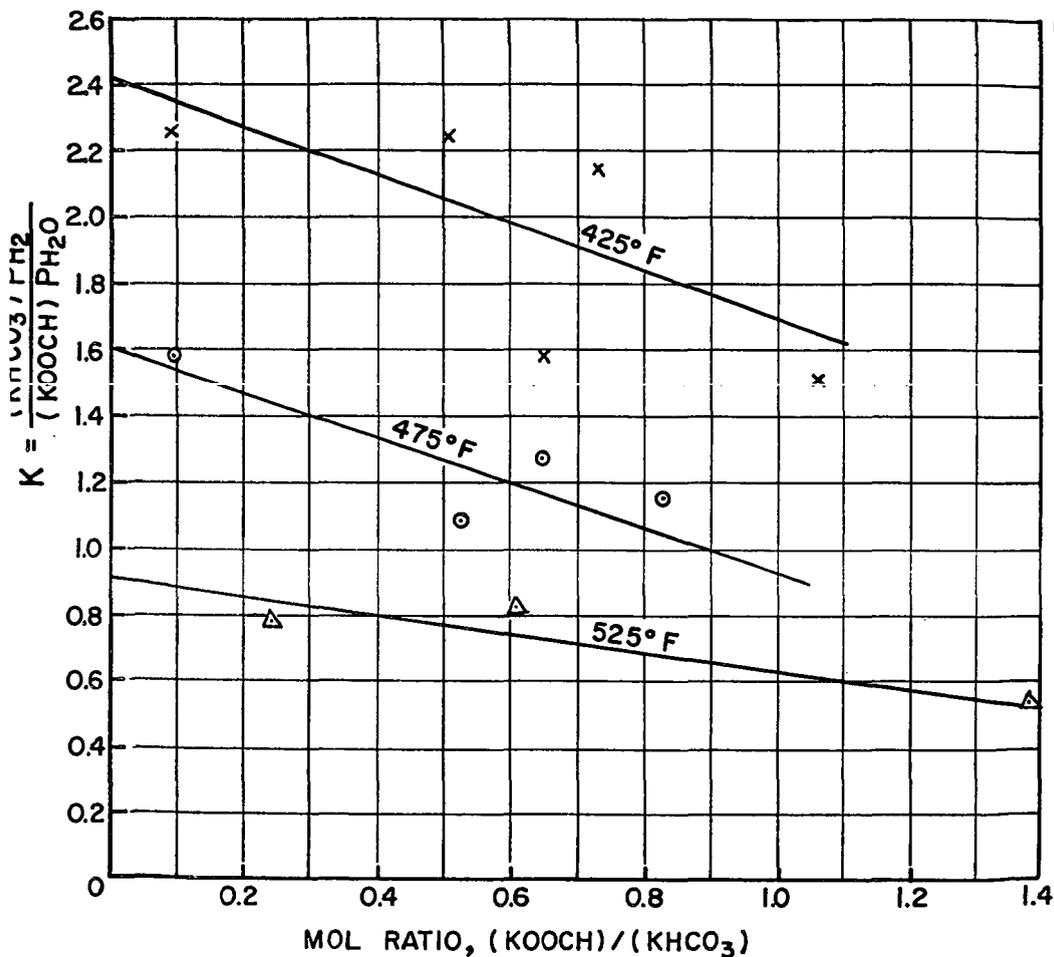


FIGURE 7
EQUILIBRIUM HYDROGEN PRESSURE
VS FRACTION KOOCH DECOMPOSED

		SMOOTHED DATA POINTS	
		TEMP. °F	P _{H₂O} -ATM
WT. % H ₂ O ≈ 57	△	525	48.9
$\frac{\text{Mols K}}{1000 \text{ gms H}_2\text{O}} = 9.0$	○	475	32.0
	x	425	17.8

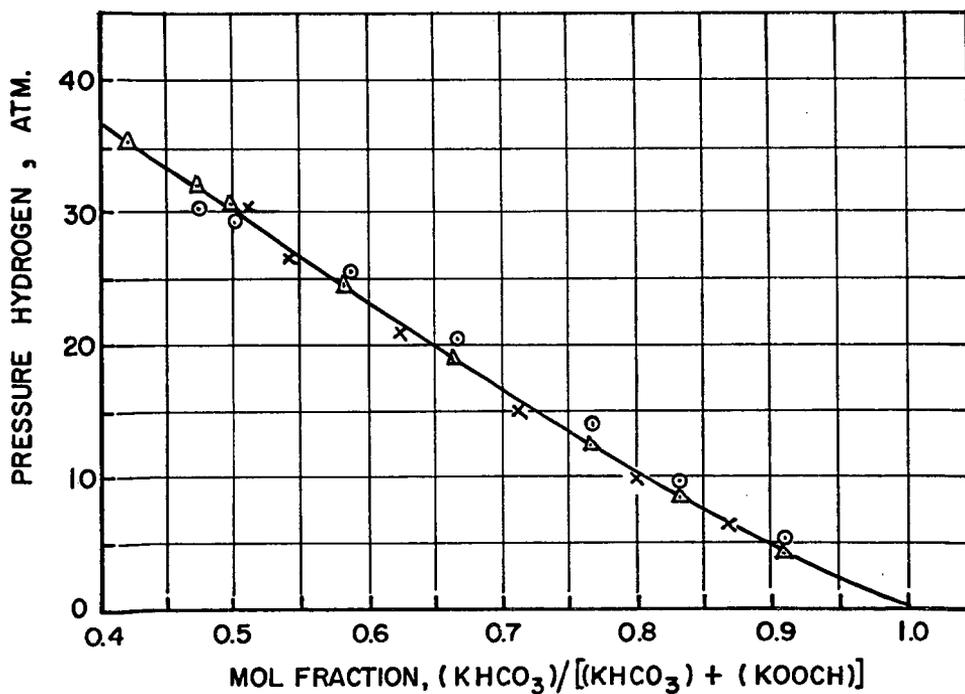


FIGURE 8

COMPARISON OF DATA ON PARTIAL
PRESSURE OF CO₂ OVER
POTASH SOLUTIONS

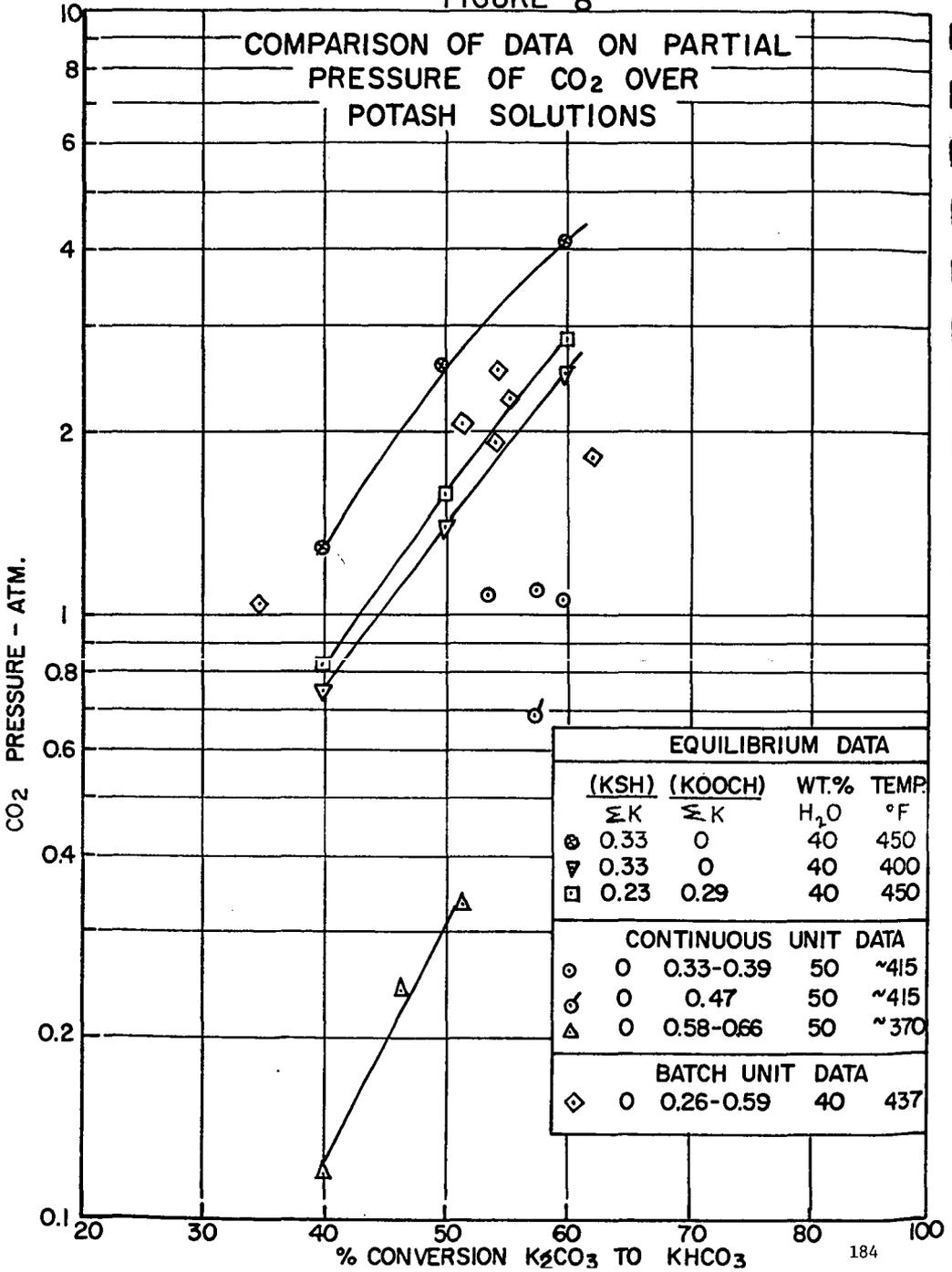


FIGURE 9
 APPROACH TO EQUILIBRIUM IN CATALYTIC
 DECOMPOSITION OF AQUEOUS KOOCH

$\frac{\text{MOLS K}}{1000 \text{ GMS H}_2\text{O}} = 12.5$

WT. % H₂O = 50.5

	TEMP. °F	P _{H₂O} -ATM.
△ EQUIL. LINE	525	22.2
○ " "	475	24.6
⊙ " "	425	27.7
EXPTL. POINTS		
△	525	22.2
○	475	24.6
x	425	27.7

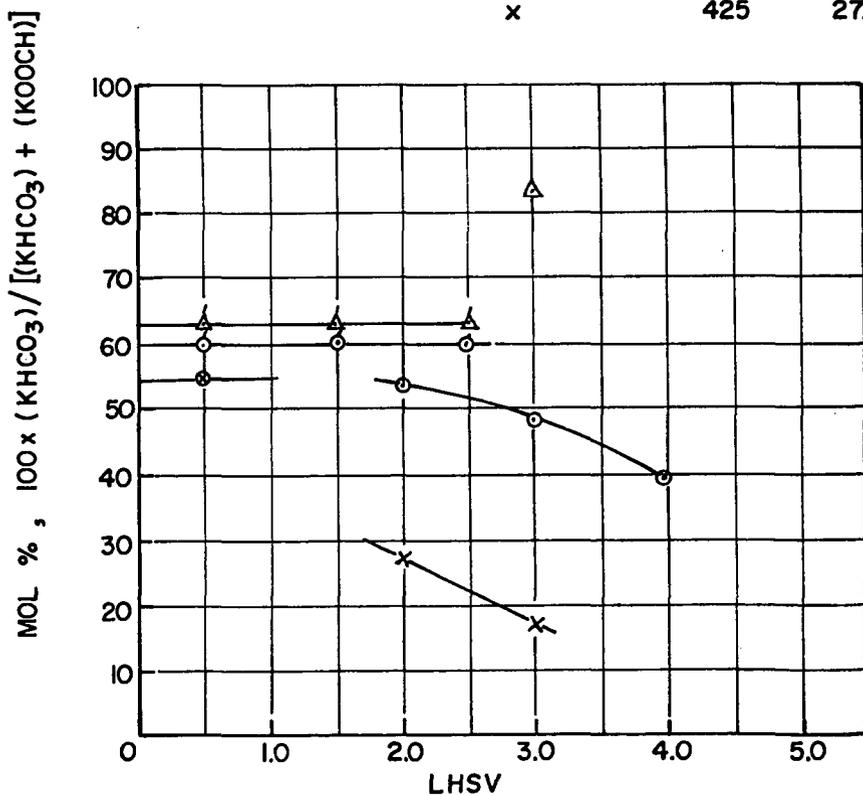


FIGURE 10
 CATALYST LIFE IN KOOCH DECOMPOSITION

TEMP. 475°F LHSV = 3 OP. PRESS. = 774 PSIA

$\frac{\text{MOLS K}}{1000 \text{ GMS H}_2\text{O}} = 12.5$ WT. % H₂O = 50.5

