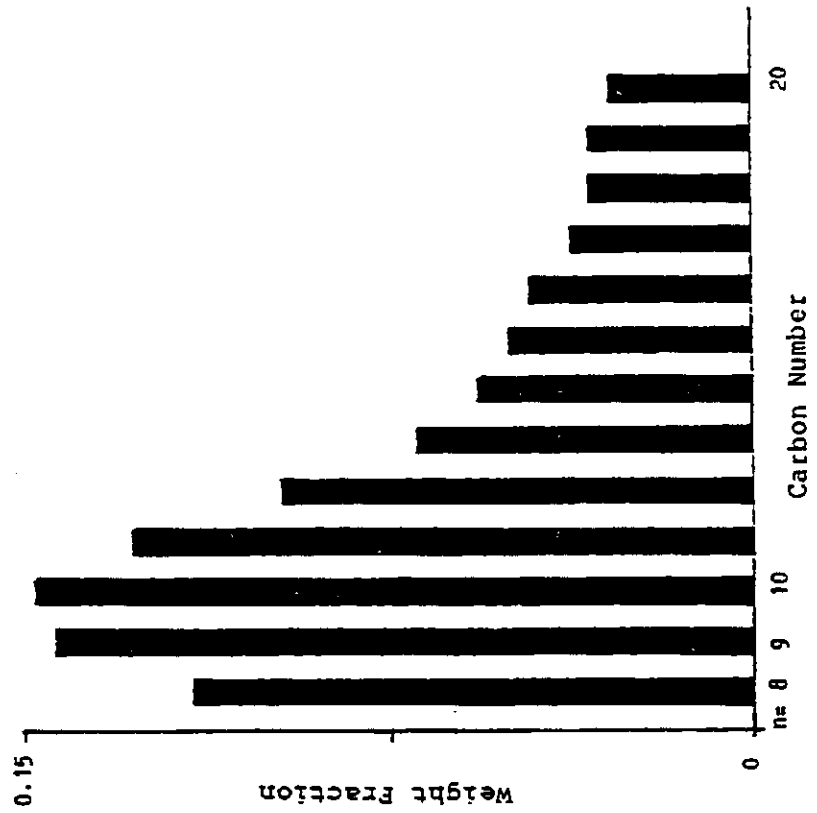

Figure 25. Liquid product C_7+ carbon number distribution for optimum verification run.

catalyst slurry, and a molar hydrogen/carbon monoxide feed ratio of 0.5.

V. Summary and Recommendations

Slurry phase catalyst development has been continued through the use of iron based Fischer-Tropsch catalysts. An alumina supported iron catalyst produced the lowest yields of all catalysts tested, perhaps due to the chemical nature of the carrier. Potassium promotion of the alumina supported catalyst improved the yields substantially, and increased the mole fractions of the higher molecular weight products. Unsupported iron catalysts achieved only moderate liquid product yields. The best iron catalyst tested was supported on kieselguhr. This catalyst produced higher yields of liquid product than any of the other iron catalysts tested, and favored the formation of lighter hydrocarbons. A copper promoter was used in all catalysts tested in order to facilitate reduction in the slurry phase.

Using the iron-kieselguhr catalyst, the best slurry liquid was found to be Chevron Refined Wax 143. Any high boiling paraffin wax should also be suitable. At reasonable temperatures, the iron catalysts do not appear to crack the wax at significant rates. Two silicone liquids, Syltherm 800 heat transfer fluid and

Dow Corning 210H fluid, disrupted the activity of the catalyst. Additionally, Syltherm 800 was unstable at synthesis conditions. Two pure paraffins, n-hexadecane and n-eicosane, did not interfere with the catalyst's activity; however, their high vapor pressures at synthesis temperatures lead to high slurry liquid attrition rates from the reactor. Finally, the use of Fischer-Tropsch product itself as a slurry liquid appears to be effective. Modifications to the slurry reactor system are required to make the use of this liquid practical.

A two level, four factor factorial study was performed to assess the importance of temperature, pressure, hydrogen/carbon monoxide feed ratio, and catalyst concentration in the slurry on the yields of liquid organic product. Temperature was found to be the most important factor, followed by the hydrogen/carbon monoxide feed ratio, catalyst concentration, and pressure. Several polynomial equations were used to represent the experimental yield data for the purposes of optimization. Two of the best fitting 16 constant models predicted the operating conditions to be close to the intersection of constraints: 300^{o}C, 187 psig, 0.5 mole ratio of hydrogen/carbon monoxide in the feed gas, and a .05 weight fraction catalyst slurry. The product

yield measured at these conditions was 118 mg/g-cat/hr. A third model predicted an interior optimum on the maximum temperature and pressure constraints, 300°C and 200 psig. The molar hydrogen/carbon monoxide feed ratio and weight fraction catalyst slurry were 1.3 and .101, respectively. Unfortunately, the predicted optimum liquid product yield of 187 mg/g-cat/hr could not be verified experimentally.

Several modifications to the existing system could be made to improve the reactor performance, and to test new ideas. A major weakness of the existing system is the limited flowrate available using the mass flow-meters. The 1 cm/s superficial velocity used during this study should be considered the lowest reasonable flowrate for a slurry phase Fischer-Tropsch reactor. Virtually all successful slurry studies reported in the literature used much higher flowrates, (up to 9.5 cm/s superficial inlet velocity), mechanical mixing of the slurry, or both. Increased flows should improve catalyst mixing, and increase gas holdups, thus enhance reactor performance. It would be interesting to have the superficial inlet velocity included as a factor in a set of factorial experiments.

At high gas flowrates, the entrainment of slurry liquid into the outlet gas will increase. Even at low flows, it is desirable to minimize this effect. A useful modification to the reactor would remove entrained liquid from the exiting gas stream. A demister above the slurry bed, or an expanded diameter reactor head could perhaps be used.

Many of the early investigators of iron based Fischer-Tropsch catalysts emphasized the importance of the proper pretreatment of their catalysts, but there have been few reports of any systematic investigations into this phenomena, particularly in slurry reactors. Also, a slurry reactor design which would allow fluidized bed operation during catalyst reduction, i.e., a narrowed reactor inlet and high temperature gaskets, combined with the pumping system available to add slurry liquid to the reactor, would allow a wider range of reduction conditions. A knowledge of the proper reduction/pretreatment method for a particular iron catalyst should lead to a more active, reliable catalyst.

The system currently in use is not practical for long term operation because it requires the constant attention of an operator. A system which could be

operated with a minimum of human supervision would be valuable in studying catalyst activity and slurry liquid integrity over time periods applicable to continuous industrial processing, (i.e., more than seven days). Such a system would require automated gas sampling and data logging (temperature, pressure, and flowrate), and should be designed as independent as possible of other laboratory functions.

There are very few promising slurry liquid candidates remaining which have not been tested. Numerous hydrocarbon liquids, silicone liquids, and synthetic fluids have been tested. As a class of compounds, chlorinated solvents may have some potential for use as slurry liquids. Their effect on catalyst performance is unknown, and obviously, it would be undesirable to have large amounts of the solvent contaminating the synthesis product.

In contrast to the slurry liquids, there are dozens of potential slurry catalysts available. From an economic standpoint, it would be difficult to justify using any metal other than cobalt or iron, but there are many different supports, promoters, and preparation methods available. The iron/copper/kieselguhr catalyst used in this study was never optimized in terms of its

composition, nor was it ever characterized. A potassium promoted version of this catalyst should be tested. A study of the effect of iron, potassium, copper, and kieselguhr content on catalyst activity could be rewarding.

There has been a great deal of interest recently in the literature in metal cluster catalysts, mainly due to their unique selectivity behavior. The catalysts are easily prepared from metal carbonyls. Iron, cobalt, and ruthenium metal cluster catalysts are active for the Fischer-Tropsch synthesis. A drawback to these catalysts is that they are easily sintered; therefore, the excellent temperature control and near isothermal operation of the slurry reactor may provide the ideal environment for the use of these catalysts.

The batch precipitation method used to prepare catalysts is very tedious and time consuming. The development of a continuous precipitator is necessary to make large batches of the catalyst, and would be useful for smaller batches as well. Impregnation methods could be considered for hardier supports, such as carbon, silica, or kieselguhr, which may not dissolve as readily as alumina in concentrated ferric nitrate solutions.

There has been no experimental work done on the hydrodynamics of slurry reactors at ASU. A pyrex or plexiglass simulator of the slurry reactor would be useful for this purpose. A hot flow simulator would be ideal for paraffin wax slurries; however, a cold flow simulator would be invaluable as well. The simulator could be used for testing different gas distributor designs, measuring minimum gas velocities required to prevent catalyst settling, and the maximum allowable velocity before slugging occurs. For modeling purposes, the simulator would be useful for measuring gas holdups, bubble size distributions, and catalyst concentrations along the length of the reactor.

Finally, it is recommended that some work be initiated on the modeling of slurry reactors. A model would be useful for design purposes, optimization, particularly beyond the range of available data, and control. The kinetics of Fischer-Tropsch reactions in general are not known, and admittedly, it is impossible to model a reactor without kinetics; nevertheless, some rate expressions over certain catalysts have been reported in the literature, along with a variety of rate forms derived from proposed mechanisms (2). Approximate

rate expressions such as those used by Deckwer (12), or lumped kinetics based on experiment could also be used.

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Appendix A. Calculation of Gas Chromatograph Response Factors.

In order to obtain quantitative results from the gas chromatograph, response factors are required for each compound detected. The response factors were determined by sampling a calibration gas of known composition. A chromatogram of such a sample appears in Figure 26, and the peaks are identified in Table 13, with the peak areas and known compositions.

Carbon dioxide is usually present in all samples, so it is used as a reference peak. The formula for calculating response factors is:

$$(RF)_i = (y_i/A_i)(A/y)CO_2 \qquad [16]$$

Where $(RF)_i$, is the response factor for component i, y is the known mole fraction of the species, and A is the peak area.

In order to perform complete material balances, it was also necessary to determine response factors for components not present in the calibration gas, such as

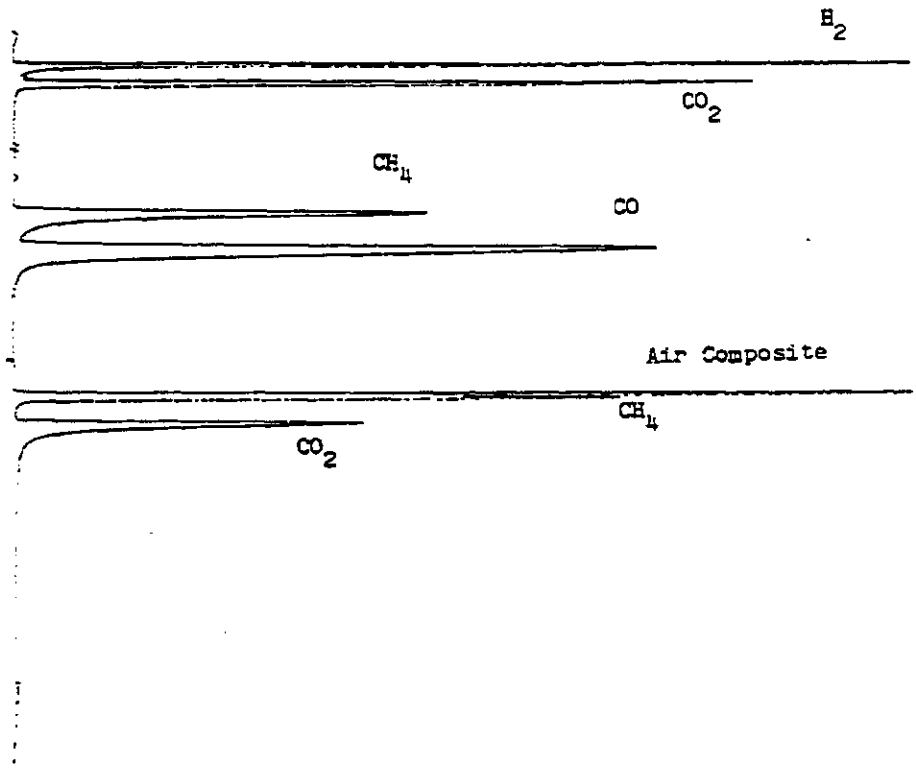

Figure 26. Chromatogram of calibration gas used to determine response factors.

Table 13. Peak areas, peak names, and composition of calibration gas used to determine response factors.

Peak #	Compound	Peak Area	Mole Fraction
1	Hydrogen	439427	0.367
2	Carbon Dioxide	515495	0.194
3	Methane	309471	0.157
4	Carbon Monxoide	656556	0.282
5	Air Composite	2264334	-
6	Methane	1317358	-
7	Carbon Dioxide	1917205	-

ethylene, ethane, propane, etc. Literature values of the response factors were used for this purpose (15). The response factors were again referenced to carbon dioxide:

$$(RF)_i = (\text{Lit RF})_i/(\text{Lit RF})CO_2 \qquad [17]$$

Where (Lit RF) is the response factor reported in the literature. The response factors for gases usually present in an outlet stream appears in Table 14.

Table 14. Calculated and literature response factors for quantitative gas chromatograph analysis.

Compound	Literature Value(15)	Literature Referenced to CO_2	Calibrated Value
Hydrogen	-	-	2.219
Carbon Monoxide	1/42	1.143	1.141
Carbon Dioxide	1/48	1.000	1.000
Methane	1/35.7	1.345	1.348
Ethylene	1/48	1.000	-
Ethane	1/51.2	0.938	-
Propene	1/64.5	0.744	-
Propane	1/64.5	0.744	-
Butene-1	1/81	0.593	-
Isobutylene	1/82	0.585	-
trans-Butene-2	1/85	0.565	-
cis-Butene-2	1/87	0.552	-
n-Butane	1/85	0.565	-
Isobutane	1/82	0.585	-
Pentene-1	1/98.5	0.487	-
trans-Pentene-2	1/104	0.462	-
cis-Pentene-2	1/98.5	0.487	-
n-Pentane	1/105	0.457	-
Isopentane	1/102	0.471	-

Appendix B. Aqueous Phase Product Analysis.

A chromatogram of the aqueous phase product from kieselguhr supported iron catalyst appears in Figure 27. The response factors for each component were taken from the literature (15). The weight fraction of each component in the sample was calculated using the equation:

$$X_i = (RF)_i A_i / \Sigma_j (RF)_j A_j \qquad [18]$$

Where $(RF)_i$ and A_i are the response factor and peak area of component i, respectively. The response factors, peak areas, and weight fractions of each component in the aqueous sample appears in Table 15.

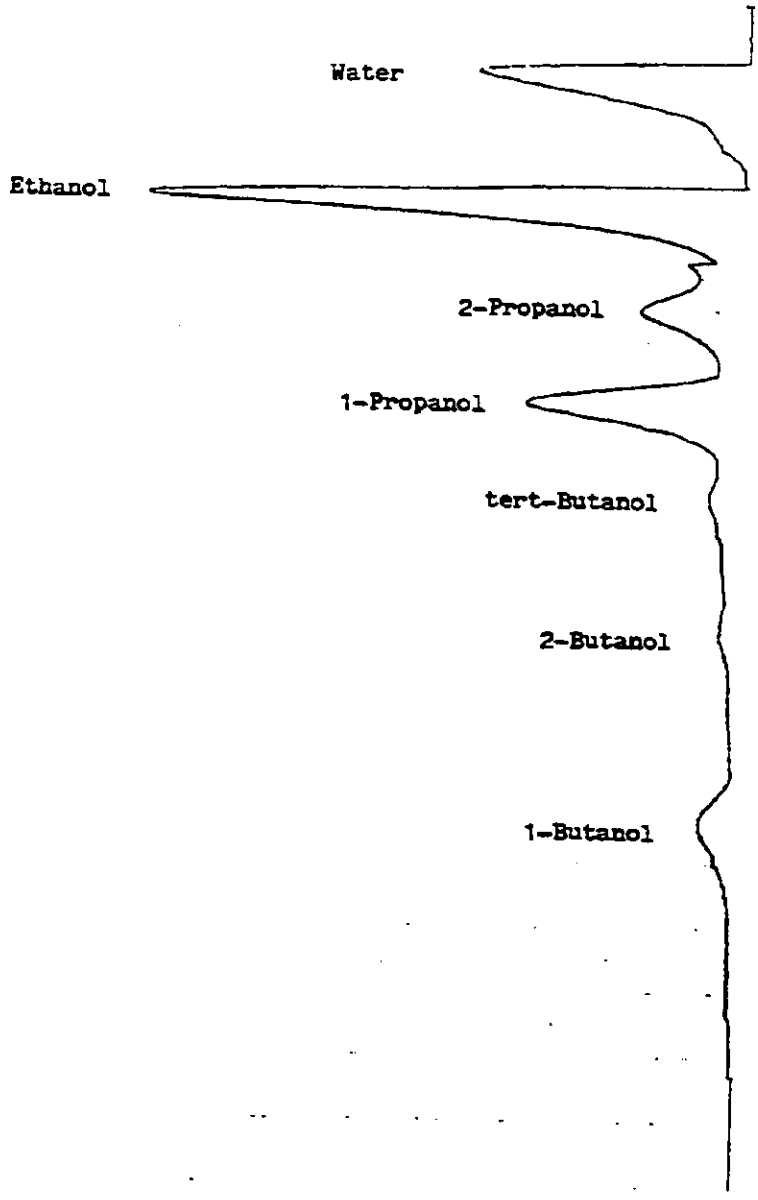

Figure 27. Aqueous phase chromatogram for iron/ kieselguhr catalyst.

Table 15. Response factors, peak areas, and weight fractions of aqueous phase sample of Figure 27.

Peak #	Compound	Response Factor(15)	Peak Area	Weight Fraction
1	Water	0.55	4640708	95.201
2	Ethanol	0.64	149317	3.063
3	2-Propanol	0.71	21812	0.447
4	1-Propanol	0.72	39412	0.809
5	tert-Butanol	0.77	9766	0.200
6	2-Butanol	0.78	2975	0.061
7	1-Butanol	0.78	10672	0.219

Appendix C. Organic Phase Prcduct Analysis.

A chromatogram of the organic phase product from kieselguhr supported iron catalyst appears in Figure 28. A flame ionization detector was used, so the response factors for each component are approximately equal. The weight fraction of each component is calculated by:

$$X_i = A_i/\Sigma_j A_j \qquad [19]$$

Where A_i is the peak area of component i. The dominant peaks appearing on the chromatogram are paraffin/olefin combinations, while the lesser peaks are isomers. The area and weight fraction of each component appears in Table 16.

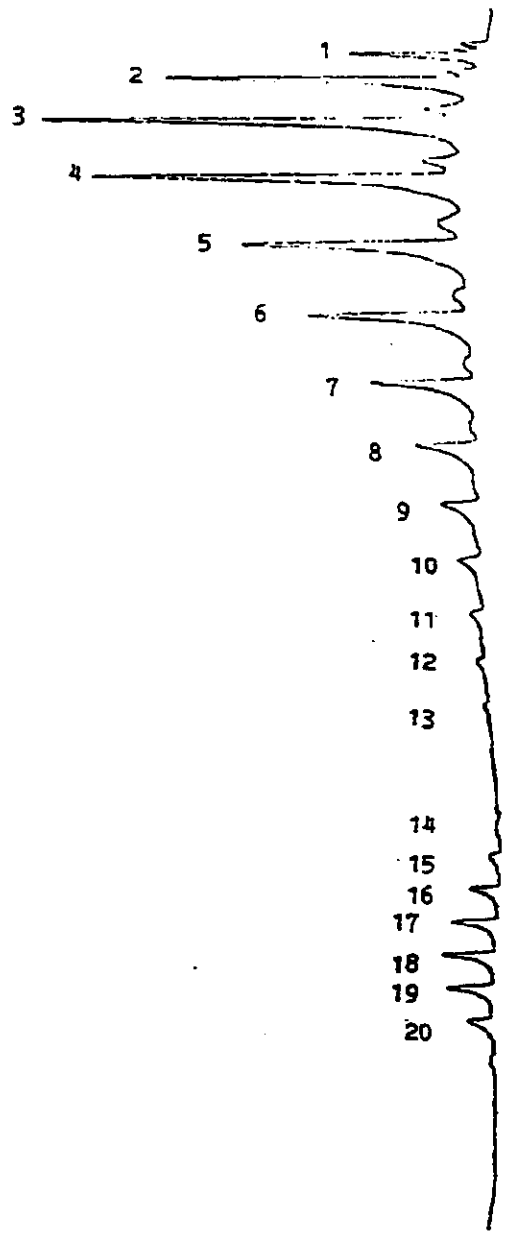

Figure 28. Organic phase chromatogram for iron/ kieselguhr catalyst.

Table 16. Peak areas and weight fractions of organic phase sample of Figure 28.

Peak #	Component	Peak Area	Weight Fraction
	$i\text{-}C_7$	76803	0.012
1	$n\text{-}C_7$	485217	0.073
	$i\text{-}C_8$	162792	0.025
2	$n\text{-}C_8$	884538	0.134
	$i\text{-}C_9$	200959	0.030
3	$n\text{-}C_9$	924450	0.140
	$i\text{-}C_{10}$	238481	0.036
4	$n\text{-}C_{10}$	739314	0.112
	$i\text{-}C_{11}$	185448	0.028
5	$n\text{-}C_{11}$	531475	0.080
	$i\text{-}C_{12}$	122402	0.019
6	$n\text{-}C_{12}$	377656	0.057
	$i\text{-}C_{13}$	97858	0.015
7	$n\text{-}C_{13}$	272090	0.041
	$i\text{-}C_{14}$	89498	0.014
8	$n\text{-}C_{14}$	274391	0.042
9	$n\text{-}C_{15}$	203715	0.031
10	$n\text{-}C_{16}$	141796	0.021
11	$n\text{-}C_{17}$	93872	0.014
12	$n\text{-}C_{18}$	50643	0.008
13	$n\text{-}C_{19}$	15696	0.002
	$n\text{-}C_{20}$	2314	0.000
14	$n\text{-}C_{21}$	34877	0.005
15	$n\text{-}C_{22}$	71538	0.011
16	$n\text{-}C_{23}$	97232	0.015
17	$n\text{-}C_{24}$	101945	0.015
18	$n\text{-}C_{25}$	84646	0.013
19	$n\text{-}C_{26}$	31605	0.005
20	$n\text{-}C_{27}$	12109	0.002
	Total	6605360	

Appendix D. Catalyst Preparation.

All iron catalysts were prepared by precipitation of ferric nitrate with ammonium hydroxide. The procedure describes the method used to make 300 g catalyst with a composition of 48 wt % Fe, 4.8 % Cu, and 47.2 % kieselguhr.

Starting materials:

Fe: 300 (0.48) = 144 g Fe (mol Fe/55.847 g)
= 2.578 mol Fe
= 2.578 mol $Fe(NO_3)_3:9H_2O$ (404 g/mol)
= 1042 g $Fe(NO_3)_3:9H_2O$

Cu: 300 (0.048) = 14.4 g Cu (mol Cu/63.546 g)
= 0.227 mol Cu
= .227 mol $Cu(NO_3)_2$ (187.56 g/mol)
= 42.5 g $Cu(NO_3)_2$

The copper nitrate used is known to contain 19% water by weight.

(42.5 g)/(1.0 - 0.19) = 52.5 g $Cu(NO_3)_2:nH_2O$

Kieselguhr: 300 (.472) = 142 g Kieselguhr

The iron and copper nitrates were dissolved in 12000 ml of distilled water, and heated to 80°C. The solution concentration was:

(1042 + 42.5)/(12000 + 1042 + 42.5)*100 % = 8.3 %

After the solution was heated, the kieselguhr was then added. While mixing vigorously, hot 1.5 M NH_4OH solution was added until the pH reached 7.0 +/- 0.1. The resulting precipitate was drained, and washed three times with 4000 ml boiling distilled water.

After the gel was thoroughly drained, its weight was approximately 2017 g. The gel was dried for 16 hours at 120°C, followed by calcination for 4 hours at 400°C. The catalyst was ground to 200 - 270 mesh. The weight of the oxidized catalyst (56 Fe_2O_3/4.9 CuO/39.1 Kieselguhr) was about 360 g. After reduction, the composition of the catalyst should be 48 Fe/4.8 Cu/47.2 Kieselguhr.

For a potassium promoted catalyst, potassium carbonate is added to the final two hot water rinses. For a 1 % promotion, referred to iron:

(144 g Fe) (0.01) = 1.44 g K are required

1.44 g K (mol K/39.102 g) = 0.0368 mol K (mol K_2CO_3/2 mol K)
= 0.0184 mol K_2CO_3 (138.2 g/mol)
= 2.54 g K_2CO_3

From experience, it is known that the drained, undried gel contains approximately 85 % by weight water. The amount of water in the gel is:

0.85 (2017 g) = 1714 g H_2O

The concentration of K_2CO_3 in the rinse is:

2.54/(1714 + 2.54)*100 % = 0.15 % K_2CO_3