HYDROPOLYMERIZATION OF ACETYLENE OVER PALLADIUM CATALYST IN FIXED BED PART I: EFFECT OF DIFFERENT VARIABLES ON THE PATTERN OF ACETYLENE CONVERSION

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ABSTRACT

The pattern of acetylene conversion in the hydropolymerization reaction over palladium catalyst in fixed bed has been studied and the effects of varying the palladium concentration and of incorporating $ZnO-Cr_2O_3$ additive in the catalyst have been determined. The effect of feed dilution with inert nitrogen on the conversion pattern has been studied. Conversion data on the hydropolymerization reaction carried over Pd-ZnO-Cr_2O_3-Kieselguhr (0.02:5.0:4.6:100) catalyst have been processed in respect of reaction temperature, space velocity and feed gas composition as variables. Results lead to the conclusions that acetylene conversion to ethylene, butadiene, and oil are primary reactions, while butenes are secondary products stemming from primarily produced butadiene.

INTRODUCTION

Since Sabatier and Senderens¹ (1899) observed the formation of acetylene hydropolymers in the nickel-catalysed reaction between acetylene and hydrogen, acetylene hydropolymerization has been the subject of numerous investigations. The reports in literature are, however, mostly of a qualitative nature with little stress on the kinetics of different reactions. The most important single reason for the obvious neglect of the acetylene hydropolymerization reaction was the slender prospect for its industrial utilisation in view of the inordinately high cost of acetylene from calcium carbide source in sharp contrast to that of ethylene. However, over the last few years, the method of hydrocarbon cracking to acetylene has undergone vast improvement due to development of highly efficient techniques of high temperature reactions, and there has also been a confident forecast of a drastic slide in the acetylene production cost. It is important to note that the cracking of hydrocarbons under efficient conditions would yield a mixture of acetylene

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and hydrogen, which could be directly used as the starting material for the hydropolymerization reaction. As such, these two processes, coupled together, open up possibilities of converting natural gas and by-product hydrocarbons into various useful olefins. In fact, it was the potential possibility of a low-cost aectylene-hydrogen mixture stemming from improved cracking techniques coupled with the inadequacy of the available information bearing on the kinetics of the metal-catalysed acetylene-hydrogen reaction, especially under streaming conditions, that prompted the authors to undertake the present investigation

Acetylene and hydrogen react $^{2-6}$ over palladium to give ethylene and ethane, with about 10 to 30% of the reacted acetylene being converted into less volatile hydrocarbons. Besides the formation of ethylene and oily hydrocarbons, considerable extent of hydrodimerization of acetylene to butadiene and butenes over palladium catalyst was reported by Takeshima⁷, Shiba⁸, and Gorin and Dereviyagina⁹.

Product distribution pattern in hydropolymerization of acetylene over palladium catalyst was reported by a few workers. The yields of ethylene, butadiene and butenes are affected ⁸ only slightly by the temperature and space velocity, but largely by the composition of the feed. With a 2: t acetylene-hydrogen mixture and employing a PdCl₂-Kieselguhr (0.01:100gm.) catalyst Takeshima ⁷ obtained acetylene conversion of 9 to 14% into butadiene, 3 to 6% into butenes, 28 to 41% into ethylene and 42 to 60% into olly hydrocarbons at 125° to 265°C. At higher temperatures of the order of 335°-340°C, Gorin and Dereviyagina⁹ obtained 11.6% conversion into butadiene and 8.2% into butenes at an overall 55% conversion of acetylene feed. Among palladium catalysts with additives $Pd-ZnO-Cr_2O_3$ -acid clay (1:260:240:10,000) was reported ⁸ to be the most active, producing 25-40% of butadiene of 85-88% purity and 45-50% ethylene and converting 20-25% of the feed into higher polymers.

The present communication deals with a study of acetylene conversion to products in fixed beds of palladium catalysts with temperature, space velocity, feed and catalyst compositions as the variables.

Catalysts

For all the catalysts Kieselguhr (Riedel), nitric acid washed and dried, was used as the support.

Pa-Kieselghur :

Catalysts were prepared with Pd in the following percentages by weight: 0.005, 0.010, 0.0182, 0.020 and 0.040.

A known weight of kieselguhr was thoroughly slurried with a calculated volume of standard PdC1, solution followed by drying on water bath. The dried mass was broken up, size graded between -28+35 Tyler mesh, and dried in an oven at 120°C, Reduction of the supported PdCl₂ to metallic Pd was left to be accomplished *in situ*, prior to its actual use. by heating in a current of hydrogen at 200°C.

Pd-ZnO-Cr2O3 - Kieselguhr :

For preparing the $Pd - ZnO - Cr_2O_3 - Kieselguhr$ (0.02, 5.0; 4.6, 100) catalyst, a known weight of kieselguhr was thoroughly mixed with a solution of zinc nitrate and chromium nitrate containing requisite quantities of zinc and chromium. Coprecipitation of zinc and chromium carbonates was done with 0.5N potassium carbonate solution. The precepitated mass was washed free of alkali, nitrate and carbonate ion;, and excess water removed by suction, after which its content of ZnO-Cr₂O₃-Kieselguhr was determined by incinerating a known mass under hydrogen atmosphere till the weight was constant. On the basis of this value, the rest of the carbonates plus kieselguhr mass was slurried with the calculated amount of a standard solution of PdCl₂. This was followed by removal of excess water by heating on a water bath and crushing and sieving to -28+35 Tyler mesh size. It was then heated in a muffle furnace at 400°C for 5 hours in order to decompose the zinc and chromium carbonates, and then finally sieved to eliminate the-35 mesh particles formed due to shrinkage and decomposition. Reduction to metallic Pd was carried out, prior to its actual use, by heating in a current of hydrogen at 200°C.

Experimental

Experimental studies in a flow system were carried out by employing a fixed bed of catalyst primarily because this permitted wide variation of space velocities. Difficulties regarding control of catalyst bed temperature arising from the high exothermicity of the hydropolymerization reaction were overcome by reducing considerably the catalyst volume. The use of a small catalyst volume, moreover, made it possible to conduct each experimental run with a fresh volume of catalyst, drawn from the same stock, thus ensuring uniform activity.

The product from acetylene hydropolymerization comprised both gaseous and liquid hydrocarbons. While the gaseous products could be directly enalysed, the liquid portion produced with a small amount of catalyst was so small in amount that it could not be assessed quantitatively by direct weighing and analysis. Resort was, therefore, taken to material balance, and to facilitate this process a definite amount of inert nitrogen was incorporated in the feed mixture.

Apparatus

The set up of an all-glass ("Pyrex") apparatus used in the present investigation is shown in Fig. 1. Acetylene obtained from commercial





acetylene cylinder was purified by bubbling through solutions of sodium bisulphite, chromic ac.d, mercuric chloride (in HCl) and alkaline pyrogallol placed in series, and then collected in a storage. Hydrogen and nitrogen, obtained from respective commercial gas cylinders were freed from the minor contents of oxygen by washing with alkaline pyrogallol solution and then mixed in predetermined proportions in a second storage. Purified acetylene and purified nitrogen-hydrogen mixture were then displaced by saturated brine from an overhead reservoir and introduced at predetermined rates through a mixing chamber into the reactor (1.D. 2.4 cm., length 15 cm.), which held a small volume (1.5 cm^3) of catalyst at its lower end, the upper portion serving as the preheater. For the purpose of analys's samples of feed gas were drawn from a point preceding the mixer, while product gas samples were taken from a point immediately following the salt ice traps which condensed out the heavier hydrocarbons (> C_4).

Products Identification

Products of acetylene hydropolymerization reaction, conducted under such conditions as to effect almost centiper cent conversion of acetylene, were stripped of oily hydrocarbons by passing through ice coolers and then absorbed in bromine in potassium bromide solution. The resulting mixture of olefin bromides, freed from excess bromine and dried over anhydrous calcium chloride, was subjected to fine fractionation in a spinning band column¹⁰ under reduced pressure. From the boiling point, refractive index and density measurements the principal fractions for palladium-catalysed products were identified to be dibromides of ethylene and butenes. The gaseous products from palladium-catalysed acetylene-hydrogen reaction also showed s'gnificant absorption in molten maleic anhydride¹¹ indicating the presence of butadiene-I, 3 which was also confirmed by isolating the latter as the corresponding tetrabromide (M. P. 118°C).

The saturated hydrocarbons present in product gases were always found by combustion analysis to have average carbon number very close to 2, ind cating thereby the predominance of ethane in the mixture.

Gas Analysis

Analysis of feed and product gases was done with a modified Orsat gas analyser prov ded with specially designed pipeties. Acetylene, butadiene-1, 3, butenes and etl-ylene were estimated in this order by means of alkaline K_2HgJ_4 .¹² molten maleic anhydride,¹¹ 88% H₂SO₄, and oleum respectively, after which hydrogen and saturated hydrocarbons were determined by fractional combustion.

Errors due to physical solubility of the unsaturated hydrocarbons in the aforesaid reagents for a fixed contact time, had been previously determined by treating them with known mixtures of pure gas samples prepared by usual chemical methods and appropriate corrections applied in the analysis of unknown samples.

RESULTS AND DISCUSSION

Conversion Calculations

Conversion results were expressed as per cent of feed acetylene going to form different products. Feed gases were prepared by having a definite proportion of nitrogen as the inert component so that from a balance of nitrogen in the feed and product gases the molar relationship, namely, moles of product gas/moles of feed gas, and hence overall conversion of acetylene, could be easily calculated.

The method of computing conversion patterns based on feed and product gas analyses is illustrated in Fig. 2.

Effect of Palladium Concentration

To investigate the effect of Pd-concentration in Pd-based catalysts four different concentrations ranging from 0.005 gm to 0.04 gm. Pd per 100 gm. of kieselguhr were used. Once-through conversions of acetylene to butadien-1.3, butenes, ethylene and oil are represented graphically in Fig. 3 for the reaction conditions indicated therein. Fresh samples (1.5 cm³ vol.) of catalysts from respective stocks were employed for experiments at different reaction temperature conditions. The conversion values corresponding to a reaction temperatue 270°C have been taken from these graphs and recorded in Table 1 to afford ready comparison. The facts revealed by the results are detailed below.

(i) Increasing Pd-concentration markedly increases the once-through conversion of acetylene to ethylene and to dimers (butadiene-1, 3 plus butenes), but the relative proportions of butadiene-1, 3 and butenes markedly alter and shift towards the latter.

(iii) Increasing Pd-concentration considerably increases the ethylene/oil ratio in the product.

Thus, the overall effect of increasing Pd-concentration in the aforesaid range is to shift the product distribution pattern towards the formation of more of ethylene and butenes and less of butadiene-1, 3, and oil.

Pd gm, of Pd/100	Р	ercentage of C ₂	H, converted to one pass)	products -	
gm of Kieselguhr	C₂H₄	C ₄ H ₆	C+H8	Oil	Total
0.005	27.0	3.5	2.0	16.0	48.5
0.010	44.0	4.0	4.0	20.0	72.0
0.020	55.0	4.4	6.5	21.0	86. 9
6 040	64.0	4.2	8.0	21.0	97 2

TABLE 1





(B) EXIT GAS (OVERALL PRODUCT)

(A) FEED CAS ANALYSIS



Effect of ZnO-Ci2O3 Addition

It was a general observation made in this investigation that ZnO-Cr₂O₃, when added in small amounts to a palladium-catalyst, markedly reduced its hydrogenating activity. For the purpose of comparison, the conversion data on the hydropolymerization reaction of acctylene over fresh samples (of 15 cm³ vol.) of two catalysts, namely, Pd-ZnO-Cr₂O₃-Kieselguhr (0.02:5.0:4.6:100) and Pd-Kieselguhr (0.02:109.6) are plotted in Fig. 4. It is seen that the main effect of ZnO-Cr₂O₃ is distinctly to depress the hydrogenating activity of palladium. This is reflected in the reduced scale of ethylene formation with higher conversion of acetylene to butadiene-1, 3, compared to butenes, through the total conversion to dimers (butadiene-1, 3 plus butenes) remains practically at the same level for both catalysts.

Effect of feed Composition

The effect of feed composition on the degree and pattern of acetylene conversion was studied by using the Pd-ZnO-Cr₂O₃-Kieselguer (0.02:5.0·4 6:100) catalyst. For this purpose, four different feed compositions were employed with C_2H_2 : H_2 : N_2 molar proportions of 5: 3: 2, 4: 4: 2, 3: 5: 2 and 2: 6:2. A fresh 1.5 cm³ volume of catalyst was used for each experiment. Space velocities studied ranged from 820 to 13120 hr⁻¹ (at N.T.P.) and the range of temperature for each space velocity was 200° to 330°C. Experimental conversion data obtained for arbitrary temperature levels within the range of to 330°C have been presented graphically (Figs. 5 and 6) by plotting the percentage of acetylene converted to butadiene-1, 3, butenes, ethylene, and oil against the corresponding reaction temperatures for different space velocities, based of the same volume (1.5 cm³) of catalyst and different rates of feed-flow

The extent of ethane formation in the above ranges of variables was found to be conspicuously low in comparison with that of ethylene. Thus, the C_2H_4/C_2H_6 ratio was always higher than 40:1, which became still higher at higher temperatures and with lower H_2/C_2H_2 ratio in the feed. The conversion values for ethane, being so low, have, therefore, been ignored, and taken along with ethylene in entirety.

Values for acetylene conversion A0 different products for selected reaction temperatures have been taken from the plots (Figs. 5 and 6) and are presented in Tables 2 to 5.

Figure 7 illustrates the distribution pattern of acetylene conversion to the four products, namely, butadiene-1, 3, butenes, exhylene and oil, at the reaction temperature of 250°C. It reveals the following facts:

(a) When extended towards zero acetylene conversion, only the butenescurve tends towards zero indicating that butenes are secondary products while the other three, butadiene-1, 3, ethylene and oil, are formed by primary reactions.



















Pattern of Acetylene conversion at Different Acetylene-Hydrogen Ratios

(b) With the increase in the ratio of H_2 to C_2H_2 the conversion to ethylene shows marked increase while that to oil falls abruptly. To afford a comparison, values of C_2H_4 /oil ratio in the products for different feed compositions at a temperature of 250°C and corresponding to 50% total conversion (once-through) of acetylene are presented in table 6.

(c) The degree of acetylene hydrodimerization to butadiene-1, 3 and butenes increasing H_2 to C_2H_2 ratio in feed as can be seen from Table 7, the data of which have been collected from Fig. 7 corresponding to 50% overall conversion of acetylene

Feed Composition $C_2H_2 50\%$; $H_2 30\%$; $N_2 20\%$ (by vol.)							
Vol. Space velocity (hr -1 at	Reaction	Percentage of C_2H_2 converted to pro (in one pass)				oducts	
N.T.P.)		C ₂ H ₄	C ₄ H ₆ -1, 3	C4H8	Oil	Tota	
	230	8.0	2.9	1.6	30.0	42.5	
	240	12.6	3.5	1.9	32.5	50.5	
820	250	16 0	4.0	2.2	35.0	57.2	
	260	19.0	4.5	2.4	37.5	63.4	
	270	21.5	4.9	25	39.0	67.9	
1640	230	5.5	2.5	1.0	24.0	33.0	
	240	8.0	2.8	1.2	25.5	37.5	
	250	10.5	3.3	1.3	27.5	42.6	
	260	13.0	3.5	1.4	30.0	47.9	
	270	15.0	3.9	1.5	32.5	52.9	
	230	3.5	1.5	0.5	17.0	22.5	
	240	5.0	1.9	0.6	20.0	27.5	
3280	250	7.0	2.3	u.7	22.5	32.5	
	260	9.0	2.7	0.8	25.0	37.5	
	270	11.5	3.3	0.9	27.0	42.7	

TABLE 2

Single-Pass Conversions of Acetylene at different Temperatures and Space Velocities.

Effect of Feed Dilution

The effect of diluting C_2H_2 - H_2 feed with an inert gas, such as N_2 , was investigated by conducting reactions under identical conditions with the same feed composition (C_2H_2 : H_2 : ratio) but having different concentrations of the added inert component. Once-through conversions obtained at different temperatures are plotted in Fig. 8. Product distribution patterns expressed as percentage of acetylene converted to different product, have been calculated for reaction temperatures of 250°C and 275°C from the corresponding conversion values taken from the plots of Fig. 8. These results, as recorded in table 8, prove that the degree of feed dilution influences the relative yields of ethylene and oil, so much so that a progressive dilution causes an increase in the yield of ethylene and decrease in that of oil, and vice-versa.

TABLE 3
Single-Pass Conversions of Acetylene at different Temperatures and Space Velocitie
Field Composition $C_{\rm He} 40\%$ \cdot H $_{\rm 2}40\%$ \cdot N $_{\rm 2}20\%$ (by vol.)

-	cou composition	0,111,107	0,	. 20/0 (0) .	,		
Vol. space velocity (hr ⁻¹ at ter	Reaction	Perc	Percentage of C ₂ H ₁ converted to Products (in one pass)				
N.T.P.)	сепр. С	C ₂ H ₄	C,Ha-1, 3	C4H8	Oil	Total	
	230	39.5	68	48	27 0	78.1	
	240	43 5	7.5	5.5	27 5	84 0	
820	250	47.0	8 0	6.0	28 5	89.5	
	260	50.0	8.2	6.1	29 0	93.5	
	270	52.7	83	6.0	29.5	96.5	
	230	29.0	6.0	3.0	23.5	61.5	
	240	32.5	6.7	4.2	26.0	69.4	
1640	250	36.0	7.3	5.0	27.5	75.8	
	260	39.0	7.7	5.2	28.5	80.4	
	270	42.0	8.0	5.0	28.0	83.0	
	230	15.5	4.2	1.4	17.0	38.1	
	240	18.0	4.8	1.8	19.0	43.6	
3280	250	21.0	5.4	2.2	22.5	51.1	
	260	24.5	5.9	2.4	24.0	56.8	
	270	27.5	6.4	2.6	25.0	61.5	
	230	8.0	2.2	0.5	10.0	20.7	
	240	12.0	2.7	0.8	15.0	30.5	
6560	250	15.0	3.2	1.1	16.5	35.8	
	260	17.0	3.7	1.4	18.5	40.6	
	270	18.5	4.3	1.7	20.0	44.5	

Fe	ed Composition:	C2H2 30	°/a; H: 50 %;	N_2 20 °/ $_{\circ}$ (by	vol)	
Vol. space	Reaction	Percentage of C ₂ H ₂ Converte		ed to Produ	icts	
(hr-1 at N.T.P)	thr ⁻¹ at N.T.P , temp. C	C₂Hł4	C4H6-1, 3	C4 H8	Oil	Tota
	230	45.5	4.0	3.6	8.0	56,6
	240	50 0	4.5	4.2	9.5	68.2
1640	250	53.5	5.0	4.6	11.5	74.6
	260	57,0	5.4	4.8	13.0	80.2
	270	60.0	57	5.0	14.0	84.7
	230	25 0	3.7	26	6.5	37.8
	240	31.5	5.0	3.0	8.5	48.0
3280	250	37.5	5.9	33	10.0	56.7
	260	43.0	6.4	36	11.5	64 5
	270	47.5	68	3.8	12 5	70.6
	230	14.0	2.4	1.3	4 5	22.2
	240	18.0	4.0	2.0	7.0	31.0
6560	250	22.0	5.2	2.6	9.2	39.0
	260	25.5	6.2	30	11.0	45.7
	270	28.5	6.7	3.2	12.0	50.4
	240	12.5	2.3	1.0	4.5	20.3
	250	15.0	3.1	1.5	6.0	25.6
13120	260	17.5	3.8	2.0	7.0	30.3
	270	19.5	4.4	2.3	8.0	34.2

TABLE 4

Single-Pass Conversions of Acetylene at different Temperatures and Space Velocities Feed Composition: C₁H₂ 30 °/₀; H₂ 50 °/₀; N₂ 20 °/₀ (by vol)

Feed	l Composition :	$C_{2}H_{2} 20 %$	H 2 60 °/o :	N ₂ 20 % (by	vol.)	
Vol space velocity (hr ⁻ ' at N.T.P.)	Reaction temp. °C	Perce C ₁ H ,	ntage of C ₂ H Spac C ₄ H ₆ -1, 3	H ₂ converted to be Velocities C 4H8	O Products Oil	Total
	230	66.5	3.3	4.9	9.0	83.7
	240	71.0	14	5.0	10 5	89,9
1640	250	75.0	3.5	5.0	12.0	95.5
	260	77 5	3.5	4.9	13.0	98.9
	270	79.0	3.4	4.6	13.0	100.)
<u></u>	230	59.0	3.5	6.2	6.5	75 2
	240	65.0	4.0	6.5	8.0	83.5
3280	250	69.0	4.4	6.7	10.0	90.1
	260	71.5	4.7	69	11.0	94.1
	270	72.5	5.0	7.0	11.5	96 0
	230	53.0	4.8	5 5	5.5	68 8
	240	60.0	5.1	5.7	7.5	78.3
6560	250	64.0	5.4	5.9	9.0	84.3
	260	66.0	5.7	6.1	9.5	87.3
	270	67.0	5.9	6.2	10.0	89.1
	230	23.0	- 4.6	2.4	3.0	33.0
	240	31.0	5.5	3.1	4 0	43.6
13120	250	39.0	6.3	3.7	5.0	54.0
	260	46.0	6.9	4.3	6.0	63.2
	270	50.5	7.4	4.8	7.0	69.7
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$\label{eq:TABLF} \begin{array}{c} T_{ABLF} \stackrel{<}{\rightarrow} \\ \text{Single-Pass Conversions of Acetylene at different Temperatures and Space Velocities} \\ Feed Composition: C_2H_2 20 \, \%_{\circ}: H_2 \, 60 \, \%_{\circ}: N_2 20 \, \%_{\circ} \ (by \ vol.) \end{array}$

TABLE O

Feed Composition	% of C2H2 converted to C2H4
$C_2H_2:H_2:N_2$	% of C2H2 converted to oil
5:3:2	0.38
4:4:2	0.93
3:5:2	2.77
2:6:2	7.15

Effect of Feed Composition on Ethylene/Oil Yield Ratio

TAI	BLE	7
1 (1)	0.0.0	

Effect of Feed Composition on Acetylene Dimerization

Feed Composition	Moles of $C_0 H_2$ converted to dimers
$C_2H_2:H_2 \cdot N_2$	100 moles of C ₂ H ₂ reacting
5:3:2	10.5
4:4:2	15.0
3:5:2	17.5
2:6:2	19.0

TABLE 8

Effect of Feed Dilution with Inert Gas on Product Distribution

Feed Composition	3	1	Moles of C2H2 c	onverted to prod	ucts
(Mole ratio) $C_2H_2: H_2: N_2$	Temp °C	C₂H,	100 moles o Dimers	f C1H, reacting Oil	A º/,
2:2:6	250	58 5	13.5	28.0	26.2
	275	53 8	196	26.6	31.6
3:3:4	250	49 .4	13.8	36.8	26.3
	275	49.1	17.7	33 2	35.0
4:4:2	250	41.9	12.0	46 1	35.8
	275	43.0	12.8	44 2	45.3

Noie: (1) A°/₂=Once-through °/₂ conversion (total) of C₃H₂ for the flow rate 2624 cm³ of C₃H₂ at N.T.P. per cm³ of catalyst per hour. (2) Dimers consist of butadience-1, 3 and butenes

. . .



Variation of Percent Conversion and Conversion Pattern of Acetylene due to feed Diffution with inert Nutrogen.

CONCLUSIONS

In the range of 0.005 to 0.040 gm. of kieselguhr, higher palladium concentration brings about a distinctly greater yield of ethylene and dimers (butadiene-1, 3 plus butenes) and less of oil.

The hydrogenating activity of palladium-catalyst is considerably suppressed by the addition of $ZnO-Cr_2O_3$, which results in a product with increased ratio of butadiene-1, 3 to butenes and reduced degree of ethylene formation.

The H_2/C_2H_2 ratio in the feed gas has a pronounced effect on the product distribution pattern, a lower ratio promoting oil formation. A higher H_2/C_2H_2 ratio in the feed gas greatly favours the formation of ethylene and dimers.

Dilution of C_2H_2 -H₂ feed gas with inert gas (N_2) augments the yield of ethylene and reduces that of oil.

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