CHAPTER IV

Here we are describing another method to obtain the value of the parameter ρ which is highly efficient than that of ordinary ratio of linear functions of observations and even highly efficient than that of the ratio of quadratic estimators as described in chapter III. The method described here is slightly different from that of described by Patterson [28].

We have seen that $\hat{r}$, the least squares estimate of ρ is obtained by solving the polynomial equation of degree 3n-11 in $\hat{r}$ and that equation can also be written as

$$r = \frac{\sum_{1}^{n-1} w_x(\hat{r}) y_x}{\sum_{1}^{n-1} w_x(\hat{r}) y_{x-1}} , \quad \left(\sum_{1}^{n-1} w_x = \sum_{1}^{n-1} x w_x = 0 \right) \quad \ldots (4.1)$$

where $w_x(\hat{r})$ are polynomials of degree 3n-12 for some specified values of $\hat{r}$. Shah [31] pointed out that when full efficiencies are not required, a useful approximation to $\hat{r}$ can be obtained very simply from

$$r' = \sum w_x y_x / \sum w_x y_{x-1} , \quad \left(\sum w_x = \sum x w_x = 0 \right) \quad \ldots (4.2)$$

where w_x are constants. In chapter II it is also described how to estimate the other parameters by fitting a partial regression of y on x and r^x. From the efficiency Table of Chapter II it can be seen that for large values of $n > 8$, the efficiencies are very low at high values of ρ. While this has been achieved some what for quadratic estimators. But for $n > 8$, this efficiencies are significantly low either for quadratic estimators for $\rho > 0.5$ or for Hartley's modified method for $\rho < 0.5$. The purpose of this chapter is to investi -gate a method which has high efficiency even for n = 12, Shah and Khatri [33].

1. Modified Method for Estimating ρ.

The modification consists of replacing w_x of (4.2) by functions $u_x + rv_x$, chosen to give as good approximations as possible to the polynomials $w_x(r)$; the resulting estimate, which will be denoted by r, is then one of the roots of the quadratic equation

$$r^2 \sum v_x y_{x-1} - r(\sum v_x y_x - \sum u_x y_{x-1}) - \sum u_x y_x = 0. \quad \ldots \quad (4.3)$$

Note the following things in deciding the which root of the equation should be taken:

(i) Positive root of the equation should be taken,

(ii) and that it should be between 0 and 1.

When n=5, the u_x and v_x can be chosen so that

$$u_x + r_i v_x \propto w_x(r_i) \quad \ldots \quad (4.4)$$

for three different values of $r_i = r_1, r_2, r_3$. The estimate r is then equal to $\hat{r}$, the least squares estimates of ρ, for each of the three values. When the r_i are taken to be 0, 0.5 and 1, the values of u_x and v_x (with arbitrary factor) are:

$$\begin{array}{lrrrr} x: & 1 & 2 & 3 & 4 \\ u_x: & 4 & -2 & -8 & 6 \\ v_x: & 11 & -13 & -7 & 9. \end{array} \qquad \ldots \qquad (4.5)$$

Note that $\sum u_x = \sum xu_x = 0$ and $\sum v_x = \sum xv_x = 0$ since

$\sum w_x = \sum xw_x = 0.$

The asymptotic efficiency of r, when y's are independent and have equal variance σ^2, is

$$\frac{\sigma^2}{\beta^2}\,\frac{(1+\rho^2)\sum_1^{n-1}(u_x+\rho v_x)^2-2\rho\sum^{n-1}(u_x+\rho v_x)(u_{x-1}+\rho v_{x-1})}{\left[\sum_1^{n-1}(u_x+\rho v_x)\ \rho^{x-1}\right]^2} \quad \ldots (4.6)$$

The corresponding variance of $\hat{r}$ is $F_{rr}\sigma^2/\beta^2$, where F_{rr} is a quantity defined in Chapter I. The ratio of these variances gives the efficiency for different values of ρ and n. Corresponding to the set given in equation (4.5) i.e. for n=5, the efficiency is very good (over 99.9%) for the whole range of ρ and hence the approximation is a good one.

Equation (4.3) can be used to provide an estimate of ρ, and the values of the u_x and v_x can also be obtained by using the method given above when $n > 5$, but since the degree of the

Polynomials $w_x(r)$ increases with n, we give here an approximate method for obtaining the u_x and v_x for n=6 to 14. These values of u_x and v_x are given in Table 4.1.

Method for $n > 5$:

$u_x + r_i v_x \propto w_x(r_i)$ gives following two equations for two values of r_1 and r_2 say,

$$u_x + r_1 v_x = p_1 w_x(r_1) \qquad \ldots \qquad (4.7)$$

$$u_x + r_2 v_x = p_2 w_x(r_2)$$

Solving these equations for u_x and v_x, we have

$$u_x = p_2 \left[r_1 w_x(r_2) - r_2 \, p \, w_x(r_1) \right] / (r_1 - r_2), \ldots \qquad (4.8)$$

$$v_x = p_2 \left[p \, w_x(r_1) - w_x(r_2) \right] / (r_1 - r_2), \text{ where } p = p_1/p_2 .$$

Now $w_x(\rho) = p_3(u_x + \rho v_x)$ gives by substituting the values of u_x and v_x from (4.8), we have

$$w_x(\rho) = p_2 p_3 \left[r_1 w_x(r_2) - r_2 p w_x(r_1) + \rho p w_x(r_1) - \rho w_x(r_2) \right] / \left[r_1 - r_2 \right]. \ldots (4.9)$$

The variance of $w_x(\rho)$ should be minimised at the third value of r say at $r=r_3$. Putting $w_x(\rho) = u_x + \rho v_x$ in equation (4.6), where $w_x(\rho)$ is given by (4.9), we have the variance of r as

$$V(r)= \frac{(1+\rho^2)\left[p^2(\rho-r_2)^2A_1+2p(\rho-r_2)(r_1-\rho)A_2+(r_1-\rho)^2A_3\right] -2\rho\left[p^2(\rho-r_2)^2B_1+2p(\rho-r_2)(r_1-\rho)B_2+(r_1-\rho)^2B_3\right]}{\left[p(\rho-r_2)C_1+(r_1-\rho)C_2\right]^2} \quad \ldots(4.10)$$

Where $A_1=\sum w_x^2(r_1)$, $A_2=\sum w_x(r_1)w_x(r_2)$, $A_3=\sum w_x^2(r_3)$,

$B_1=\sum w_x(r_1)w_{x-1}(r_1)$, $B_2=\frac{1}{2}\left[\sum w_x(r_1)w_{x-1}(r_2)\right.$

$\left.+\sum w_{x-1}(r_1)w_x(r_2)\right]$, $B_3=\sum w_x(r_2)w_{x-1}(r_2)$

$C_1=\sum w_x(r_1)\rho^{x-1}$ and $C_2=\sum w_x(r_2)\rho^{x-1}$.

Differentiating equation (4.10) with respect to p, we have solving for p:

$$p=\frac{(r_1-\rho)\left[(1+\rho^2)(A_3C_1-A_2C_2)-2\rho(B_3C_1-B_2C_2)\right]}{(\rho-r_2)\left[(1+\rho^2)(A_1C_2-A_2C_1)-2\rho(B_1C_2-B_2C_1)\right]} \quad \ldots(4.11)$$

The values of $w_x(r_1)$ and $w_x(r_2)$ can be calculated by the following formula as described in Chapter III,

$$\underline{w}=\left\{\left[V^{-1}-V^{-1}X(X'V^{-1}X)^{-1}X'V^{-1}\right]\underline{R}_0\right\} \ldots(4.12)$$

where X, $\underline{R}_0$ and V are defined in chapter III. Thus $\underline{w}$ is determined by equation (4.12) at a particular value of ρ_0.

Procedure for preparing table:

Choose any two values of r_1 and r_2. Calculate $w_x(r_1)$ and $w_x(r_2)$ from equation (4.12). Find value of p from equation (4.11) at the third value of ρ say r_3. Thus the vector $w_x(r_1)$ and $w_x(r_2)$ and ps is known. Calculate u_x and v_x from the following equations (in arbitrary constant factor):

$$u_x = r_1 w_x(r_2) - r_2 p\, w_x(r_1) \quad \text{and}$$

$$v_x = p\, w_x(r_1) - w_x(r_2) \; .$$

Description of the Table :

Table (4.1) gives three sets of values for different sets of r_1, r_2 and r_3 . The following sets are chosen:

(a) $r_1=0.5$, $r_2=1$ and $r_3=0$,

(b) $r_1=0$, $r_2=0.5$ and $r_3=1$.

The third set (c) is obtained from these sets in such a way that the efficiencies at $\rho=0$, and $\rho=1$ are nearly equal. For n=7, the over all efficiencies for the set (c) is above 99.0%. For n=14, the efficiency for the set (a) is low for $\rho < .5$ and also low for set (b) for $\rho > .5$. While the third set is balanced, it has high efficiencies between $\rho=.3$ and $\rho=.7$, and has over all efficiency equal to 93%. While in quadratic estimators the over all efficiency for n=8 is 93% . Thus we can see that the efficiency has much increased. But it is expected that the efficiency will be considerably low for $n > 20$. This will be discussed in Chapter V.

Examples:

The following examples are taken from a Ph.D. thesis submitted to the Chemical Engineering School by Bruce McCarty [1]. The Chemisorption of Oxygen on a Silver Catalyst (rate and equilibrium data) was studied at 350°, 400°, 450° and 500°F pressures having values of 50, 100, 200 and 400 mm. Hg. were studied at each temperature. Measurements were taken at 3, 5, 7, 10, 15, 20, 25, 30, 40, 50 and 60 minutes after the Oxygen was admitted into the balance housing. The rate data for Oxygen had previously been fitted to the integrated form of the Langmuir equation* for adsorption with dissociation.

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* The integrated Langmuir equation is

$$\log \frac{(2av_a+b-\sqrt{b^2-4ac})\,(b+\sqrt{b^2-4ac})}{(2av_a+b+\sqrt{b^2+4ac})\,(b-\sqrt{b^2-4ac})} = t\sqrt{b^2-4ac},$$

where $a=(K_1Po_2-K_2)/V_m^2$, $b=-(2K_1Po_2)/V_m$, c=K_1Po_2 and where K_1 and K_2 are the rate constants for adsorption and desorption, Po_2 is the pressure of Oxygen, V_m=volume of gas adsorbed in a monolayer and V_a is the volume of gas adsorbed corresponding to any particular pressure.

For the pmactical use of data, we have used the volume of gas adsorbed corresponding to pressure 50 mm. Hg at 400^{0} and 450^{0}F at equal intervals of time.

(i) At 400^{0}F temperature and 50 mm. Hg. pressure the data is as follows:

Time	$y=(v_a)(10^2)$ (1)	Eq.(4.13) (2)	Using non-linear regression (3)
0	1.00	0.9975	0.9975
1	1.18	1.1911	1.1912
2	1.31	1.2981	1.2982
3	1.37	1.3590	1.3591
4	1.37	1.3953	1.3955
5	1.43	1.4187	1.4190

Referring to table for n=6, the set no.(c), we have from equation (4.3):

$$-11.0010\, r^2 + 0.1389\, r + 3.0349 = 0 .$$

The positive root of the equation is found to be 0.5316. Using this value of ρ=0.5316, other parameters can be obtained by partial regression of y on $(0.5316)^x$ and x. Hence the fitted regression is

$$y=1.3925 + 0.0086x - 0.3950\,\rho^x \quad \ldots \quad (4.13)$$

The expected values are tabulated in column 2.

<u>Remarks</u>: The non-linear regression curve given above can be fitted by the method described by Hartley [12]. The following set was obtained using a non linear regression programme with modified computational procedure:

	$\hat{\alpha}$	$\hat{\beta}$	$\hat{\delta}$	$\hat{\rho}$
Values from Eq.(4.13):	1.3925	0.0086	-0.3950	0.5316
Values using non-linear regression :	1.3916	0.0088	-0.3941	0.5308 .

The estimates obtained by both the methods agrees to two decimal places. The expected values obtained by using non-linear regression are given in column (3). The observed values by both the methods agrees to three decimal places.

Example 2: At 450°F temperature and 50 mm. Hg. pressure the data is as follows:

Time	$y=(v_a)(10^2)$ (1)	Eq.(4.14) (2)
0	1.12	I.I200
1	1.21	I.2I02
2	1.25	I.2494
3	1.28	I.2805
4	1.31	I.3I03
5	1.34	I.3398.

Referring to table for n = 6 (set c), we have equation (4.3) as:

$$-2.8680\, r^2 - 1.3611\, r + 0.2935 = 0,$$

which gives the positive root of the equation as 0.1610. Therefore the regression equation is found to be

$$y = 1.1923 + (0.0295)x - (0.0723)\,(0.161)^x \quad \ldots (6.14)$$

Table 4.1

Values of u_x and v_x for n=6 to 14.

n=6							
(a)	u_x:	12.09	-11.11	-8.69	2.35	5.36	
	v_x:	12.91	1.11	-21.31	-12.35	19.64	
(b)	u_x:	17.26	-17.26	-8.63	0.00	8.63	
	v_x:	28.06	-1.11	-48.02	-12.90	33.96	
(c)	u_x:	29.35	-28.37	-17.32	2.35	13.99	
	v_x:	40.97	0.01	-69.33	-25.25	53.60	
n=7							
(a)	u_x:	14.84	-9.20	-12.36	-2.54	4.76	4.50
	v_x:	10.16	9.20	-12.64	-22.46	-4.76	20.50
(b)	u_x:	27.20	-21.76	-13.60	-5.44	2.72	10.88
	v_x:	42.18	21.22	-63.36	-55.90	6.10	49.76
(c)	u_x:	42.04	-30.96	-25.96	-7.98	7.48	15.38
	v_x:	52.34	30.42	-76.00	-78.36	1.34	70.26

n=8

(a)	u_x:	25.12	-10.00	-20.80	-10.36	2.84	7.88	5.32
	v_x:	9.88	20.00	-4.20	-29.64	-27.84	2.12	29.68
(b)	u_x:	38.70	-25.80	-18.06	-10.32	-2.58	5.16	12.90
	v_x:	54.40	51.60	-64.28	-89.76	-43.44	28.88	62.60
(c)	u_x:	63.82	-35.80	-38.86	-20.68	0.26	13.04	18.22
	v_x:	64.28	71.60	-68.48	-119.40	-71.28	31.00	92.28

n=9

(a)	u_x:	61.06	-12.98	-47.56	-34.66	-5.71	13.79	16.45	9.61
	v_x:	8.94	47.98	17.56	-40.34	-69.29	-43.79	18.55	60.39
(b)	u_x:	66.15	-37.80	-28.35	-18.90	-9.45	0.00	9.45	18.90
	v_x:	34.30	103.60	-41.90	-101.60	-83.70	-20.60	46.50	63.40
(c)	u_x:	127.21	-50.78	-75.91	-53.56	-15.16	13.79	25.90	28.51
	v_x:	43.24	151.58	-24.34	-141.94	-152.99	-64.39	65.05	123.79

n=10

(a)	u_x:	43.88	-2.96	-30.77	-28.52	-11.62	4.01	10.87	9.61
	v_x:	-1.88	30.96	23.77	-9.48	-38.38	-42.01	-17.87	18.39
	u_x:	5.50							
	v_x:	36.50							

(b)	u_x:	62.72	-31.36	-24.64	-17.92	-11.20	4.48	2.24
	v_x:	74.16	120.92	-38.52	-118.76	-120.80	-70.04	4.52
	u_x:	8.96	15.68					
	v_x:	69.48	79.04					

(c)	u_x:	106.60	-34.32	-55.41	-46.44	-22.82	-0.47	13.11
	v_x:	72.28	151.88	-14.75	-128.24	-159.18	-112.05	-13.35
	u_x:	18.57	21.18					
	v_x:	87.87	115.54					

n=11

(a)	u_x:	55.91	3.01	-34.38	-38.37	-22.29	-2.73	9.93
	v_x:	-10.91	32.99	37.38	6.87	-30.21	-49.77	-41.43
	u_x:	13.12	9.95	5.85				
	v_x:	-10.12	26.05	39.15				

(b)	u_x:	74.52	-33.12	-26.91	-20.70	-14.49	-8.28	-2.07
	v_y:	81.16	155.24	-17.78	-118.00	-141.62	-109.44	-45.06
	u_x:	4.14	10.35	16.56				
	v_x:	28.52	84.10	82.88				

(c)	u_x:	130.43	-30.11	-61.29	-59.07	-36.78	-11.01	7.86
	v_x:	70.25	188.23	19.60	-111.13	-171.83	-159.21	-86.49
	u_x:	17.26	20.30	22.41				
	v_x:	18.40	110.15	122.03				

n=12

(a)	u_x:	72.48	11.22	-38.16	-50.07	-35.85	-12.87	5.91
	v_x:	-22.98	33.78	51.66	26.07	-16.65	-50.13	-58.41
	u_x:	15.03	15.03	10.65	6.63			
	v_x:	-39.03	-1.53	34.35	42.87			
(b)	u_x:	85.65	-34.26	-28.55	-22.84	-17.13	-11.42	-5.71
	v_x:	86.90	187.52	4.90	-111.12	-152.74	-137.76	-87.18
	u_x:	0.00	5.71	11.42	17.13			
	v_x:	-19.00	48.98	94.96	84.54			
(c)	u_x:	158.13	-23.04	-66.71	-72.91	-52.98	-24.29	0.20
	v_x:	63.92	221.30	56.56	-85.05	-169.39	-187.89	-145.59
	u_x:	15.03	20.74	22.07	23.76			
	v_x:	-58.03	47.45	129.31	127.41			

n=13

(a)	u_x:	94.20	22.70	-41.61	-63.54	-52.52	-27.05	-2.02
	v_x:	-39.20	32.30	66.61	48.54	2.52	-42.95	-67.98
	u_x:	14.14	19.31	16.75	11.66	7.98		
	v_x:	-64.14	-34.31	8.25	43.34	47.02		
(b)	u_x:	96.25	-35.00	-29.75	-24.50	-19.25	-14.00	-8.75
	v_x:	91.30	217.80	27.90	-100.40	-156.50	-156.60	-119.50
	u_x:	-3.50	1.75	7.00	12.25	17.50		
	v_x:	-61.20	4.70	65.40	102.30	84.80		

(c)	u_x:	190.45	-12.30	-71.36	-88.04	-71.77	-41.05	-10.77
	v_x:	52.10	250.10	94.51	-51.86	-153.98	-199.55	-187.48
	u_x:	10.64	21.06	23.75	23.91	25.48		
	v_x:	-125.34	-29.61	73.65	-145.64	131.82		

n=14

(a)	u_x:	141.77	44.40	-51.22	-91.41	-84.48	-53.01	-16.95
	v_x:	-70.27	32.60	95.22	86.41	31.98	-32.99	-81.05
	u_x:	10.90	25.20	26.92	21.33	15.14	11.41	
	v_x:	-96.90	-77.70	-31.92	22.67	61.86	60.09	
(b)	u_x:	137.28	-45.76	-39.52	-33.28	-27.04	-20.80	-14.56
	v_x:	124.38	318.60	65.52	-173.77	-202.15	-218.42	-185.90
	u_x:	-8.32	-2.08	4.16	10.40	16.64	22.88	
	v_x:	-123.84	-46.90	32.68	101.40	139.07	109.33	
(c)	u_x:	279.05	-1.36	-90.74	-124.69	-111.52	-73.81	-31.51
	v_x:	54.11	351.20	160.74	-27.36	-170.17	-251.41	-266.95
	u_x:	2.58	23.12	31.08	31.73	31.78	34.29	
	v_x:	-220.74	-124.60	0.76	124.07	200.93	169.42	

Table 4.2

Efficiencies of the estimates of ρ obtained from equation (4.3) using u_x and v_x of Table 4.1

ρ	n=7 (a)	(b)	(c)	n=14 (a)	(b)	(c)
0.0	91.2	100.0	98.8	60.8	100.0	85.7
0.2	98.5	99.5	99.7	86.4	95.5	94.0
0.3	99.6	99.7	100.0	94.6	96.4	98.7
0.4	99.9	99.9	100.0	98.9	98.7	99.1
0.5	100.0	100.0	100.0	100.0	100.0	100.0
0.6	100.0	99.9	100.0	98.5	97.4	99.0
0.7	99.9	99.6	100.0	98.7	89.6	96.1
0.8	99.8	98.9	99.9	98.8	86.9	92.2
1.0	100.0	97.7	98.8	100.0	73.4	84.3