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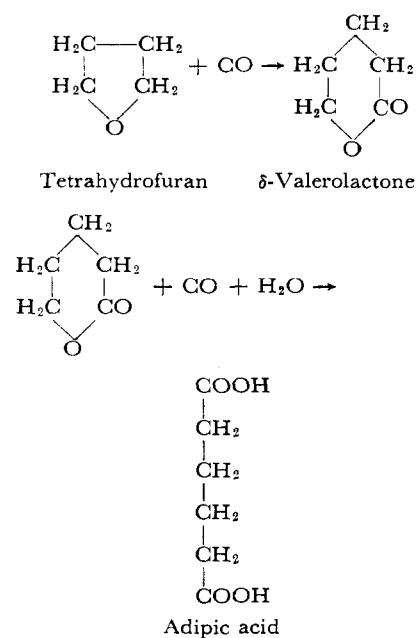
High Pressure Synthesis of Delta-Valerolactone and Adipic Acid

ADIPIC ACID, used in products such as nylon, plasticizers, and resins, is now made commercially by oxidizing cyclohexane. However, because furfural may be obtained from agricultural wastes—e.g., rice bran, corncobs, oat hulls—a new process using tetrahydrofuran, carbon monoxide, and water may be used in the future.

δ-Valerolactone also is becoming increasingly important because of its use in making polyamides. It has been synthesized in Germany (6), but data on operating conditions are not available. Adipic acid has been synthesized from carbon monoxide, water, and tetrahydrofuran, using nickel carbonyl catalyst in the presence of iodine, nickel iodide, or organic iodine derivatives (9, 10, 13). It was suggested that formation of hydroiodic acid might play an important part in the synthesis, but the proposed scheme of reaction can be considered only tentative. The scheme of conversion may also involve the intermediate formation of δ-valerolactone which then may be converted to adipic acid. If this were true, the two broad steps in the reaction would be

$$
\underset{\text{Tetrahydrofuran}}{\overset{\text{H}_2\text{C}\text{---}\text{CH}_2}{\underset{\text{H}_2\text{C}\quad\text{CH}_2}{\diagdown\text{O}\diagup}}} + \text{CO} \rightarrow \underset{\delta\text{-Valerolactone}}{\overset{\text{CH}_2}{\underset{\text{H}_2\text{C}\quad\text{CO}}{\diagup\text{H}_2\text{C}\quad\text{CH}_2\diagdown}}}
$$

$$
\overset{\text{CH}_2}{\underset{\text{H}_2\text{C}\quad\text{CO}}{\diagup\text{H}_2\text{C}\quad\text{CH}_2\diagdown}}\!\diagdown\!\text{O}\!\diagup + \text{CO} + \text{H}_2\text{O} \rightarrow
$$

$$
\underset{\text{Adipic acid}}{\overset{\text{COOH}}{\underset{\text{COOH}}{|\;\text{CH}_2\;|\;\text{CH}_2\;|\;\text{CH}_2\;|\;\text{CH}_2\;|}}}
$$

Data supporting this reaction, however, are completely lacking. Therefore, to obtain more information about this synthesis, the reaction mechanism and operating conditions were studied.
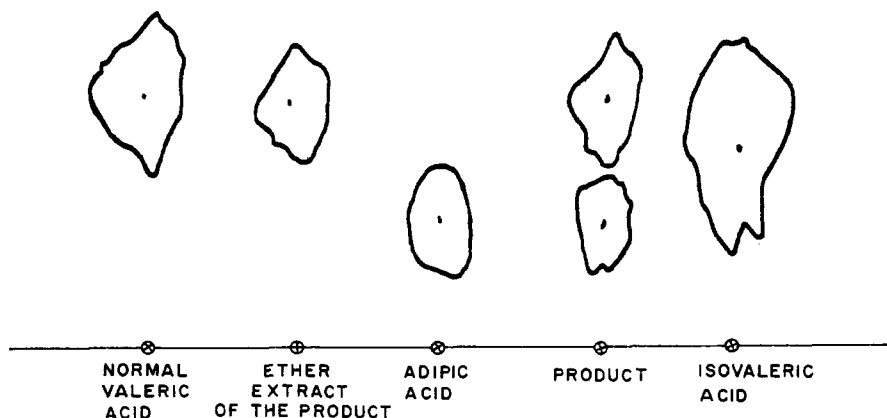

Figure 1. δ-Valerolactone synthesis. Adipic and n-valeric acid were detected in the product by the paper chromatographic technique (8). Ethanol–concentrated ammonia–water in a ratio of 80:4:16

Table I. A Nickel Iodide–Silica Catalyst and a Temperature of 200° C. are Optimum for Synthesizing Adipic Acid

(Init. press., 2500 p.s.i.)

React. Temp., ° C.	Conversion of Tetrahydrofuran, %, to		
	Adipic acid	n-Valeric acid	δ-Valero-lactone
Metal-Support Ratio, 30:70; React. Temp., 200° C.			
NiCl₂-S		2.1	0.6	1.1
NiBr₂-S		5.4	0.7	2.1
NiI₂		5.2	0.8	1.7
NiI₂-Ka		6.5	1.1	1.7
NiI₂-P		8.5	0.6	1.3
NiI₂-K		11.3	0.6	1.6
NiI₂-S		19.7	1.1	2.9
CoI₂-S[a]		10.4	1.1	2.1
FeI₂-S[a]		6.2	0.7	2.3
Metal-Support Ratio 40:60			
NiI₂-S	100	4.2	0.9	1.3
	150	13.5	1.0	1.7
	175	17.4	1.1	2.1
	200	23.0	1.2	3.3
	225	18.6	1.1	2.7
	250	14.6	1.3	2.2
	300	5.5	1.8	1.0
CoI₂-S	150	3.7	0.7	1.0
	175	8.4	0.9	1.1
	200	10.4	1.1	2.1
	225	7.7	1.0	1.6
	250	4.9	1.1	1.5
FeI₂-S	150	2.9	0.6	0.9
	175	5.0	0.6	1.1
	200	6.2	0.7	2.3
	225	4.2	0.5	1.7
	250	2.8	0.5	1.2

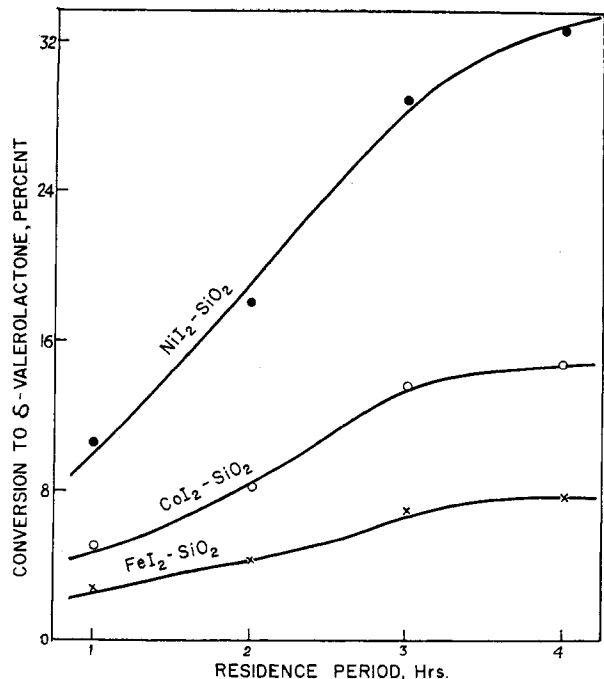K = kieselguhr; Ka = kaolin; S = silica; P = pumice. [a] Metal support ratio, 40:60.

Figure 2. δ-Valero-
lactone synthesis. Bulk
of the reaction was com-
plete in about 3 hours:
about 29% conversion
using a nickel iodide-
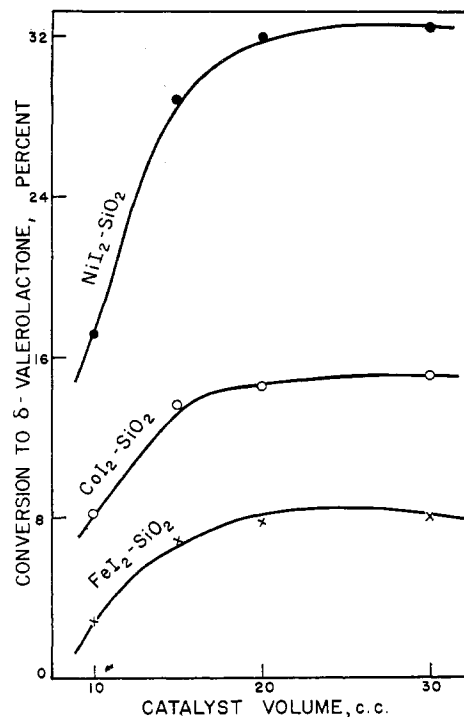silica catalyst

▶

Figure 3. δ-Valero-
lactone synthesis. The
maximum catalyst
volume needed is 15 ml.,
using a reaction pressure
of 4600 p.s.i. at 200° C.

Experimental

A 140-ml. high pressure bomb was
used, which was basically similar in de-
sign to one previously described (2).
Also, the procedure has been described
(4). Tetrahydrofuran was of pure
Merck quality, and carbon monoxide,
prepared from commercial formic acid
and sulfuric acid was purified by passing
through alkaline pyrogallol. The cata-
lysts, nickel chloride, bromide, and
iodide, and also cobalt and iron iodides,
were supported on silica gel, pumice,
kaolin, and kieselguhr. Methods of
preparation have been reported (1, 4,
5). Unless otherwise stated, data are
given for a 15-ml. catalyst volume, 10-
ml. of tetrahydrofuran, and a residence
period of 3 hours.

The gaseous products obtained con-
sisted of carbon dioxide, hydrogen, and
saturated hydrocarbons in addition to
the unreacted carbon monoxide. Gas
analysis was done by the usual method,
and saturated gaseous hydrocarbons were
estimated to consist wholly of methane.

Formic acid in the product was esti-
mated by distilling at 100° C. and oxi-
dizing the distillate with a standard
solution of potassium permanganate.
The residue from the distillation was
extracted with ether, and acidity of the
ether extract was used to determine
n-valeric acid. Residue from the ether
extraction was further extracted with
ethyl alcohol, and this extract was ti-
trated with a standard alkali solution to
estimate adipic acid. δ-Valerolactone
was determined by refluxing a portion
of the reaction product for 3 hours with
standard alkali and determining the
change in acidity.

Initial detection of adipic acid and
n-valeric acid (Figure 1) was carried

out by the paper chromatographic tech-
nique (8). Presence of δ-valerolactone
was confirmed by preparing δ-hydroxy
n-valeric hydrazide.

Discussion

δ-Valerolactone Synthesis. When
synthesizing δ-valerolactone, the liquid
product obtained contained δ-valero-
lactone and unreacted tetrahydrofuran.
When water was present, adipic, formic,
and n-valeric acids together with
unreacted water, were also present. It
has been reported that when water is
present, α- and γ-methyl butyrolactone,
isovaleric, methyl glutaric, and ethyl
succinic acids together with cyclo-
pentanone are also produced (10).
However, these by-products were not
present in appreciable quantities.

For the catalysts supported on silica,
nickel iodide was the most active and

iron iodide the least active. This agrees
with results obtained in carboxylic acid
and ester synthesis (3, 5, 11). At
temperatures of 150° to 300° C. and
constant initial pressure of 2500 p.s.i.,
which means that the amount of carbon
monoxide introduced into the sys-
tem was constant, conversion to δ-
valerolactone passes through a maxi-
mum at 200° C. Above and below this
temperature, there is a gradual fall in
yield (Table V).

When temperature was kept constant at
200° C. and pressure was varied from 2000
to 7500 p.s.i., conversion to δ-valero-
lactone rose with increasing pressure,
but the rise became less rapid as higher
pressures were attained (Table V).
A pressure of 4500 p.s.i. seemed opti-
mum. The bulk of the reaction was
completed in about 3 hours, and the

Table II. Yield Increases with Higher Pressures up to 4500 P.S.I.[a]

(Adipic acid synthesis)

Catalyst on SiO₂	Press., P.S.I.		Conversion of Tetrahydrofuran, % to		
	Initial	Max.	Adipic acid	n-Valeric acid	Lactone
NiI₂	1000	2000	9.6	0.9	2.5
	1500	2700	12.7	1.2	2.8
	2500	4500	23.0	1.2	3.3
	3000	5400	23.6	0.8	3.3
	4000	7200	25.2	0.7	3.4
CoI₂	1000	2000	3.9	0.7	1.8
	1500	2700	5.5	0.8	2.0
	2500	4500	10.4	1.1	2.1
	3000	5400	10.8	0.7	2.2
	4000	7200	11.3	0.5	2.8
FeI₂	1000	2000	2.7	0.6	1.3
	1500	2700	3.8	0.7	2.0
	2500	4500	6.2	0.7	2.3
	3000	5400	7.1	0.9	3.0
	4000	7200	7.7	0.9	3.0

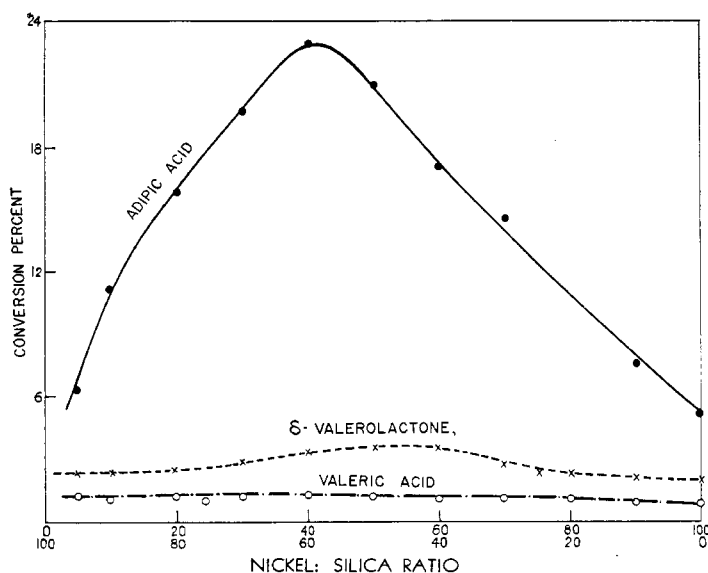[a] Metal support, 40:60; reaction temp., 200° C.

Figure 4. Adipic acid synthesis. Maximum conversion occurs with a nickel iodide–silica catalyst having a metal-support ratio of 40:60. Conversion to *n*-valeric acid and δ-valerolactone was small and not entirely independent of catalyst concentration. However variations were not large
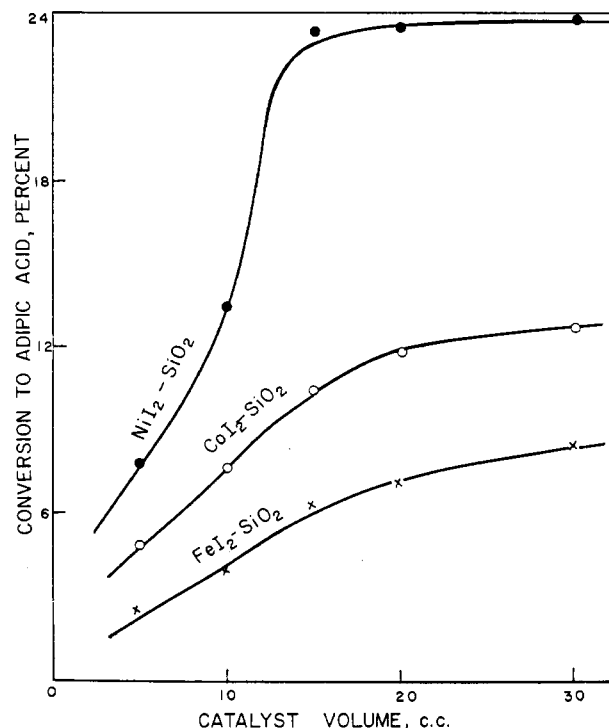

Figure 5. Adipic acid synthesis. For each of the iodide-silica catalysts, a 15-ml. volume is sufficient for maximum conversion
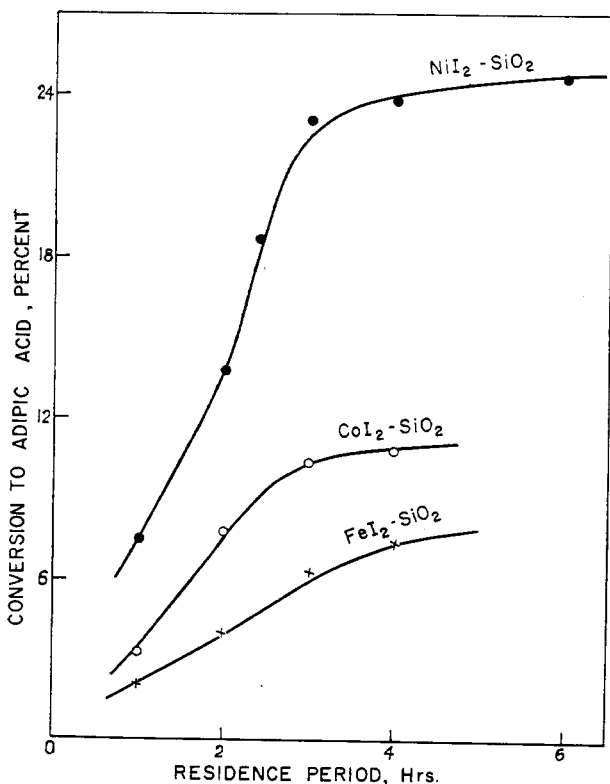

Figure 6. Adipic acid synthesis. Prolonging the residence period beyond 3 hours increases conversion but little

maximum catalyst volume needed was 15 ml. (Figures 2 and 3).

Adipic Acid Synthesis. Compared to yields obtained from uncatalyzed reactions, those using reduced nickel, cobalt, and iron were low. Nickel iodide supported on silica gel was the most efficient, and supported catalysts were more effective than those which were not supported (Table I). Catalyst life was affected but little during the 3-hour duration of each run (Table III). Because of their high activity, only iodide-silica catalysts were used in later experiments.

When temperature was kept constant at 200° C. and reaction (maximum) pressure was varied from 2000 to 7200 p.s.i., the yield of adipic acid rose rapidly up to about 4500 p.s.i. At higher pressures the rise was slow (Table II).
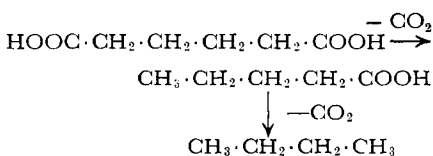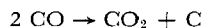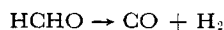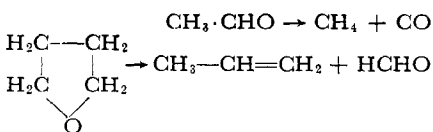
When 10 to 15 ml. of water were used with a nickel iodide–silica of 15 ml. and 10 ml. of tetrahydrofuran at a temperature of 200° C. and a reaction pressure of 4500 p.s.i., maximum conversions to adipic acid were obtained. The tetrahydrofuran–water molar ratio corresponding to these volumes was 0.22 to 0.33. Thus, 3 to 5 moles of water were required for each mole of tetrahydrofuran. This is much in excess of the theoretical value.

For best yields, products should be released at the reaction temperature. For reactions carried out at 200° C., and released at 100° C., yield decreased from 23.0 to 15.5%. When the products were released at 25° C., yield was only 7.5%.

The optimum conversion of tetrahydrofuran to adipic acid (Figures 4 and 5) was obtained with nickel iodide–

Table III. Catalyst Activity Is Retained with Use[a]

(Catalyst, NiI_2-SiO_2; NiI_2-silica ratio, 78:22)

Catalyst	Conversion of Tetrahydrofuran, %, to			Selectivity for Adipic Acid, %
	Adipic acid	*n*-Valeric acid	δ-Valerolactone	
Fresh	23.0	1.2	3.3	83.6
Once used	22.2	1.1	3.1	84.1
Twice used	21.5	1.1	3.0	84.0
Thrice used	21.2	1.1	3.0	83.8

[a] Metal support ratio, 40:60; init. press., 2500 p.s.i., reaction press., 4500 p.s.i., reaction temp., 200° C.

silica gel (78:22) at a temperature of 200° C. and a pressure of 4500 p.s.i., using 15 ml. of catalyst, 10 ml. of water, and 10 ml. of tetrahydrofuran. After 3 hours, the yield was 23.0% (Figure 6).

An increase in temperature or a decrease in pressure favored decomposition of tetrahydrofuran and adipic acid (Table IV); however, less carbon dioxide was produced from tetrahydrofuran when the pressure was decreased. The decomposition processes may be represented by

$$\begin{array}{c} H_2C\text{—}CH_2 \\ | \quad\quad | \\ H_2C \quad CH_2 \\ \diagdown O \diagup \end{array} \rightarrow CH_2{=}CH_2 + \begin{array}{c} H_2C\text{——}CH_2 \\ \diagdown O \diagup \end{array}$$

$$\begin{array}{c} H_2C\text{——}CH_2 \\ \diagdown O \diagup \end{array} \xrightarrow{\text{isomerization}}$$

$$CH_3 \cdot CHO \rightarrow CH_4 + CO$$

$$\begin{array}{c} H_2C\text{—}CH_2 \\ | \quad\quad | \\ H_2C \quad CH_2 \\ \diagdown O \diagup \end{array} \rightarrow CH_3\text{—}CH{=}CH_2 + HCHO$$

$$HCHO \rightarrow CO + H_2$$

$$2\,CO \rightarrow CO_2 + C$$

$$HOOC \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH \xrightarrow{-CO_2}$$
$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$$
$$\downarrow {-CO_2}$$
$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$$
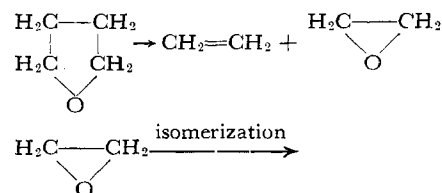
Olefins may further decompose into smaller unsaturated units and ultimately to hydrogen and elementary carbon. Hydrogen may partly hydrogenate to unsaturated fragments and further to saturated hydrocarbons such as methane and ethane. The first five equations agree with those of Klute and others (7) who identified acetaldehyde and formaldehyde as intermediate products formed in low and high pressure decomposition. In decomposition of adipic acid, *n*-butane formed may crack ultimately to various products such as olefins, saturated hydrocarbons, hydrogen, and elementary carbon. However, only some of these reactions take place with nickel iodide–silica catalyst, depending on temperatures and pressures.

Conclusions

In both syntheses, optimum temperature, pressure, residence period, and catalyst volume are identical (Table V). Moreover, the sum of conversion of tetrahydrofuran to δ-valerolactone and adipic acid in one synthesis was often similar to that for δ-valerolactone in the other. This seems to provide some evidence for Reppe's suggestion that conversion to δ-valerolactone is the first step in adipic acid synthesis. In the second step, most of the lactone formed is converted to adipic acid, and speed of the reaction seems to be governed by that of the first step.

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Table IV. High Temperatures and Pressures Cause Decomposition

(Catalyst, NiI₂-SiO₂; metal-support ratio, 40:60)

Temp., ° C.	Pressure, P.S.I. Init.	Max.	CO₂	CO	Unsatd. HC as C₂H₄	Saturated hydrocarbons (as CH₄)	Total	H₂/CH₄ Ratio
				Tetrahydrofuran, 10 Ml.				
150	2500	4200	1.1	1.4	5.3	0.9	8.7	1.0
200	2500	5000	1.8	2.8	7.3	1.6	13.5	0.7
250	2500	5800	2.3	4.1	9.7	2.0	18.1	0.7
300	2500	6700	3.1	5.2	12.5	2.9	23.7	0.6
200	1500	3000	1.2	3.8	9.5	1.8	16.3	0.8
200	2500	5000	1.8	2.8	7.3	1.6	13.5	0.7
200	3500	6800	2.0	2.2	5.5	0.9	10.6	0.9
				Adipic Acid, 3.5 G.				
150	2500	4300	5.0		2.5	1.6	9.1	1.6
200	2500	5200	6.4		3.4	1.9	11.7	1.7
250	2500	6000	13.4		6.3	2.6	22.3	1.8
300	2500	7000	17.5		8.3	3.5	29.3	1.6
200	1500	3200	10.3		4.4	3.1	17.8	1.5
200	2500	5200	6.4		3.4	1.9	11.7	1.7
200	3500	6900	5.0		3.0	1.6	9.6	1.7

Table V. Yields[a] of Adipic Acid and δ-Valerolactone Are Similar

(Metal-support ratio, 40:60)

Temp., ° C.	Catalyst on SiO₂	Initial Press., P.S.I.	Reaction Press., P.S.I.	Adipic Acid Adipic acid	Lactone	Total	δ-Valerolactone Lactone
150	NiI₂	2500	3900	13.5	1.7	15.2	20.1
	CoI₂	2500	3900	3.7	1.0	4.7	7.4
	FeI₂	2500	3900	2.9	0.9	3.8	4.2
200	NiI₂	1000	2000	9.6	2.5	12.1	14.3
	CoI₂	1000	2000	3.9	1.8	5.7	5.0
	FeI₂	1000	2000	2.7	1.3	4.0	2.1
	NiI₂	1500	2700	12.7	2.8	15.5	18.2
	CoI₂	1500	2700	5.5	2.0	7.5	8.5
	FeI₂	1500	2700	3.8	2.0	5.8	3.9
	NiI₂	2500	4500	23.0	3.2	26.2	28.8
	CoI₂	2500	4500	10.4	2.1	12.5	13.6
	FeI₂	2500	4500	6.2	2.3	8.5	6.8
	NiI₂	3000	5400	23.6	3.3	26.9	29.6
	CoI₂	3000	5400	10.8	2.2	13.0	15.3
	FeI₂	3000	5400	7.1	3.0	10.1	7.6
	NiI₂	4000	7200	25.2	3.4	28.6	32.1
	CoI₂	4000	7200	11.3	2.8	14.1	15.9
	FeI₂	4000	7200	7.7	3.0	10.7	8.0
250	NiI₂	2500	5200	14.6	2.2	16.8	14.5
	CoI₂	2500	5200	4.9	1.5	6.4	5.2
	FeI₂	2500	5200	2.8	1.2	4.0	3.0

[a] Yield in % tetrahydrofuran conversion.