

## THE REACTION OF CO<sub>2</sub> WITH COKE ON SPENT CATALYSTS

W. P. Hettinger, Jr., J. F. Hoffman and S. M. Kovach

Ashland Petroleum Company  
Research and Development Department  
Ashland, Kentucky 41114

### Introduction

The processing of residuum from the bottom of the crude oil barrel into transportation fuels has become both economically attractive and necessary as crude oil has become heavier and more expensive. In processing these heavier feedstocks, as with Ashland Oil's RCC<sup>SM</sup> heavy oil conversion process, more coke is produced than in conventional FCC operations. Tremendous amounts of heat are produced during the regeneration of coked catalysts. Conventional methods to moderate the temperature in the regenerator of a circulating fluidized bed include controlling operational parameter-(eg. cat/oil, feed preheat, and reactor temperature), direct addition of steam and/or water to the riser or regenerator (U.S. Patent 4,405,444), the use of multi-bed regenerators (CAN Patent 1,137,455), the use of steam coils in the regenerator, and the incomplete combustion of coke (U.S. Patent 4,354,923). Because of economic constraints on varying the operational parameters and metallurgical limitations, and temperature stability of catalysts, especially when loaded with Ni and V,<sup>(1)</sup> a practical limit to the regenerator temperature exists. In a further effort to lower the amount of heat produced in the regenerator, other solutions to the problem were sought.

### Program

One new approach not mentioned above was to employ the Boudouard Reaction, one of the principle reactions studied for many years in the steel industry as related to iron production. This paper reports the results of a study of the partial regeneration of spent (coked) cracking catalysts with CO<sub>2</sub> (Boudouard Reaction). It also reports a second and equally interesting reaction which was uncovered in the course of this work. The second reaction is called the H-reaction, which is the reaction of the hydrogen associated with the carbon in the "catalytic coke" with CO<sub>2</sub> to produce CO and water. Catalytic coke on spent catalyst is a species which is 92-97%C and 3-8%H and contains minor amounts of sulfur and nitrogen.

The reaction of carbon with CO<sub>2</sub> to produce carbon monoxide (Boudouard Reaction)<sup>(2,3,4)</sup> is endothermic as is well known. The H-reaction also appears to be slightly endothermic. The H-reaction would lower the amount of heat produced in the regenerator if it could be achieved at the exit temperature of the reactor (1000°F) or at a slightly higher temperature in the spent catalyst stripper section by removing hydrogen before it can undergo combustion. Carbon dioxide in the flue gas from an FCC or RCC unit is available for these reactions.

The pertinent thermodynamics parameters for the coke-O<sub>2</sub> and coke-CO<sub>2</sub> reactions are presented in Table 1.<sup>(5)</sup> The equilibrium constant of the Boudouard Reaction does not favor the formation of CO at temperatures below 1300°F. In order to obtain significant amounts of CO, temperatures above 1800°F are required.<sup>(6)</sup> By use of a promoter, substantial

amounts of CO can be produced at 1350-1400°F. The most active promoters of the Boudouard Reaction are salts of the alkali metals and the metals of Group VIII in the periodic table<sup>(6)</sup>. The H-reaction was found to proceed at a much lower temperature than the Boudouard Reaction, hence, it is of greater interest because of the lower temperature at which it can be initiated.

In past investigations of the Boudouard Reaction, the fate of the hydrogen present in very small quantities in coke has not apparently been of interest. In this investigation, an attempt has been made to confirm the production of the H<sub>2</sub>O formed by the reaction of the hydrogen-associated coke with CO<sub>2</sub>, and to determine the lower temperature limit where this reaction can be utilized.

The objectives of this work were to determine:

- 1) The metals which would promote the Boudouard Reaction, but do not adversely affect the activity and selectivity of the cracking catalyst.
- 3) The effect of nickel and vanadium, which are deposited on the catalyst during the cracking reaction, as promoters of the Boudouard Reaction.
- 3) The fate of hydrogen during the reaction of coke with CO<sub>2</sub>.
- 4) The temperature at which the H-reaction initiates.

### Experimental

Catalyst samples which had been coked in a commercial circulating fluidized bed unit were impregnated with aqueous solutions of a metal salt (chloride or nitrate) by the incipient wetness technique. The solutions were prepared with the appropriate metal salt to give 1.0 wt% as the element on the catalyst after impregnation. The impregnated catalysts were then dried at 300°F for at least three hours before testing. The activity of the impregnated catalyst to promote the Boudouard Reaction was determined by measuring the amount of carbon which had reacted during a 30 minute test. The reaction was performed at 1400°F in a 1" ID Vycor reactor with a thermocouple well in the dense phase of the fluidized bed. Twenty grams of the coked metal impregnated catalyst was heated to the reaction temperature and equilibrated in a stream of helium. Carbon dioxide was then introduced at a constant rate of 1.7 scfh. The CO concentration in the product gases was monitored at regular intervals by gas chromatography. After each test, the catalyst was cooled in helium and the %C left on the catalyst was determined.

In order to study the H-reaction, the catalyst was heated to 600°F for one hour in helium to remove physically adsorbed water. After cooling to 100°F in helium, the catalyst was heated in CO<sub>2</sub> to the desired temperature, 900-1400°F, over a 30 minute period, and then held at this temperature for an additional 30 minutes. The moisture content of the gas stream was measured over the entire 60 minute test with a Shaw hygrometer (Model SH), which was equipped with a gold spot sensor. This sensor was capable of measuring dew points between -58°F and +68°F. The amount of H<sub>2</sub>O produced during the H-reaction was calculated by integrating the plot of dew point vs. time.

## Results and Discussion

### A. Metal Promoters for the Boudouard Reaction

A wide variety of metal salts have been tested as possible promoters for the Boudouard Reaction. The results of the screening tests showed that the most active promoters were the alkali metals and the metals of Group VIII, which agreed with earlier literature reports<sup>(6)</sup>. The screening tests consisted of impregnating each metal onto the coked catalyst and then determining its activity by measuring the %C on the catalyst after contact with CO<sub>2</sub> for 30 minutes. Each promoter was tested on the same spent catalyst (Ni+V = 5900 ppm). The metals were divided into three classes (Table 2) based on their activity to promote the Boudouard Reaction.

An important requirement of this investigation was that the cracking activity and selectivity of the catalyst should not be affected by the promoter. The cracking activity and selectivity were measured by a standard micro-activity test (MAT)<sup>(7)</sup>. The catalyst was calcined at 1100°F for 2 hours to remove all of the coke before running the MAT. The highest activity promoters in Table 2 were evaluated by the MAT. The results of the MAT evaluation are given in Table 3. Catalyst cracking activity is related to the MAT conversion, and selectivity is related to the coke producing factor (CPF) and hydrogen producing factor (HPF). The CPF or HPF is defined as the ratio of the amount of coke or hydrogen produced during the test to the amount produced with a standard catalyst at the same conversion.

A comparison of Table 2 and 3 showed that while the lithium promoted catalyst exhibited the highest activity for the Boudouard Reaction, the cracking activity, as expected, had been drastically reduced by the addition of lithium. Of the other promoters in the highest activity group of Table 2, copper and strontium were selected for further study based on the MAT results. Barium was also selected for further study even though on the standard catalyst the activity was in the lowest class. At Ni+V concentrations greater than 8000 ppm, barium did exhibit substantial activity for the Boudouard Reaction.

Lithium because of its deleterious effect on cracking activity, and rhodium, because of its cost, were not considered possible promoters at the 1.0 wt% and 0.5 wt% levels, respectively. In an attempt to use these high activity promoters, the effect of promoter concentration on activity was examined (Table 4). At feasible concentrations of the promoters (0.1% Li and 5 ppm Rh), their activity had decreased to a level comparable to the unpromoted reaction.

The effect of the contaminant metals (Ni and V), which were deposited on the catalyst during the cracking reaction, on the activity of the various promoters was investigated. Each promoter was impregnated on various spent equilibrium catalyst samples. The results of these tests were plotted as %C on catalyst after the 30 minute test (normalized to 1.0 wt% C initially on the catalyst) versus Ni+V (Figures 1-3 for copper, strontium and barium promoted catalysts, respectively). Each metal promoted the Boudouard Reaction to a greater extent as the concentration of Ni+V increased. The promoter and the contaminant metals exhibited a synergistic effect on increasing the rate of the Boudouard Reaction. The circled data points in Figures 1-3 supported the idea of synergism. These data points were the results of experiments in which the Ni/V ratio on the catalyst was equal to one. The

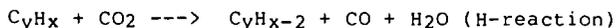
remaining data points, those that fall on the curves, were the results of experiments in which the promoters were impregnated on catalysts with Ni/V ratios equal to 1/3. The circled data points showed, at comparable metals levels, that less coke had undergone reaction with CO<sub>2</sub> in the catalysts with lower vanadium concentrations. Vanadium, when impregnated on spent catalyst, exhibited moderate activity (35% carbon removal on a catalyst containing 5900 ppm Ni+V). Nickel and vanadium, deposited on the catalyst during the cracking reaction, promoted the Boudouard Reaction only when the total concentration of these metals was greater than 8000 ppm. At Ni+V concentrations, above 15,000 ppm, these metals promote the Boudouard Reaction to the same extent as the highest activity metals (see Figure 4).

In the previous experiments, the catalyst samples were impregnated with the promoter after the catalyst was deactivated with coke. However, in a commercial process, the promoter could be deposited on the catalyst during manufacture or during the process. A series of experiments were performed to compare the activity of barium impregnated on the catalyst before coking and after coking. The conclusion was that barium exhibited a higher activity when the metal was impregnated before the catalyst was deactivated (see Table 5).

A series of experiments were performed to test the ability of a barium promoted catalyst (Ni+V = 12,600 ppm) to maintain activity over ten coking-regeneration cycles. Each cycle consisted of, first, coking the regenerated catalyst with a vacuum gas oil at 900°F, then allowing the spent catalyst to react with CO<sub>2</sub> for 30 minutes at 1400°F, and finally, regenerating the catalyst with air at 1200°F. In Figure 5, the peak height of CO in the GC analysis of the product gas stream plotted against the number of coking-regeneration cycles. The amount of CO in the gas stream was determined 5 times (at 2, 9, 16, 23 and 30 minutes) during coke-CO<sub>2</sub> reaction. The activity of the promoter decreased slightly over the ten cycles.

#### B. H-Reaction Studies

Coke has a composition in the range of 92-97% C and 3-8% H<sup>(8)</sup> with trace amounts of nitrogen and sulfur. In previous reports<sup>(9,10)</sup> on promoting the Boudouard Reaction, the hydrogen in coke has either been assumed not to react with CO<sub>2</sub> or not mentioned. Hydrogen in the coke on spent catalyst was calculated to be responsible for 15-25% of the heat generated during the regeneration of catalyst spent. In this investigation, the hydrogen in coke was found to react with CO<sub>2</sub> to produce water according to the reaction sequence:



While the enthalpy change for this reaction has not been determined, it is believed to be considerably more endothermic than for the combustion reaction. By allowing the H-reaction to occur, the amount of hydrogen which must undergo combustion in the regenerator section of a fluidized reactor system would be decreased, thus, less heat would then be produced in the regenerator.

With a hygrometer inserted into the product gas stream line, the amount of water in the product gas stream, as measured by the dew point (in

°C), was determined. The concentration of water in the gas stream was determined by the equation:

$$\log (\text{H}_2\text{O in ppm}) = 13.33 - 261.3/\text{Dew Point } (^\circ\text{K})$$

A comparison of the amount of  $\text{H}_2\text{O}$  produced during the reaction of  $\text{CO}_2$  with a coked and a regenerated catalyst is given in Figure 6. The difference in the two plots is a measure of the amount of water produced by the H-reaction. The water observed in the dew point plot of the regenerated catalyst is attributed to catalyst dehydroxylation at  $1400^\circ\text{F}$ . With this technique, the amount of hydrogen in coke on a catalyst is found to be between 3-10%. The range in this value is the result of uncertainty in the amount of hydrogen in the coke which did not react during the 30 minute test.

### C. Initiation Temperature of the H-Reaction

One of the potentially useful aspects of the H-reaction is that it could be made to occur in the reactor (spent catalyst) stripper of the  $\text{RCC}^{\text{SM}}$  process unit. The temperature of the catalyst in the stripper is usually between  $900$ - $1050^\circ\text{F}$ . The thermodynamics of the H-reaction as compared to the water gas shift reaction indicates that hydrogen in coke will react at temperatures within this range. Carbon dioxide could easily be used either in place of or in conjunction with steam as a stripper gas. The advantage of reacting hydrogen in the stripper in the  $\text{RCC}^{\text{SM}}$  process unit is apparent from the data in Figure 7. This figure shows the relationship for a particular set of unit operating conditions between Conradson carbon in the feed, the water addition to the riser, and the hydrogen content in the coke in order to maintain the  $\text{RCC}^{\text{SM}}$  process unit in heat balance at a  $\text{CO}_2/\text{CO}$  ratio in the flue gas equal to one. By lowering the hydrogen content in coke, feedstocks with higher Conradson carbon values can be processed with the heat balance being maintained in the RCC unit.

The temperature at which a measurable amount of water is produced by the H-reaction has been determined. The initiation temperature was determined by a series of temperatures in which the catalyst was heated to a predetermined temperature (eg.,  $900^\circ$ ,  $1000^\circ$ ,  $1400^\circ\text{F}$ ) in  $\text{CO}_2$  and the amount of water produced during the  $\text{CO}_2$  reaction was measured. Before each test, the catalyst was heated to  $600^\circ\text{F}$  in an attempt to remove physically adsorbed water. The results of these experiments are shown in Figure 8. The set of dew point plots show that substantially more water is produced at  $1000^\circ\text{F}$  and  $1400^\circ\text{F}$  than at  $900^\circ\text{F}$ . Temperatures between  $800^\circ$ - $900^\circ\text{F}$  give identical dew point plots to the one at  $900^\circ\text{F}$ . These data indicate that the rate of the H-reaction becomes measurable between  $900^\circ$  and  $1400^\circ\text{F}$ . The source of the water in the dew point plots obtained at reaction temperature below  $900^\circ\text{F}$  is believed to be adsorbed water.

A series of experiments in a product distribution unit (PDU) were performed to quantify the amount of water produced by the H-reaction. The PDU is a homogeneous fluid bed reactor which uses a liter of catalyst. The larger volume of catalyst allows for a more accurate determination of the water produced by the hydrogen reaction. The catalyst was heated in the reactor at  $1250^\circ\text{F}$  in dry  $\text{O}_2$  free  $\text{N}_2$  overnight to remove all adsorbed and chemical water. The catalyst was then coked with a reduced crude oil and the entrained hydrocarbons were stripped from the catalyst with  $\text{N}_2$ . At this point,  $\text{CO}_2$  was introduced into the reactor, at either  $1000^\circ$  or  $1100^\circ\text{F}$ . The product gases from the H-reaction were

monitored for their water content continuously. After two hours, the CO<sub>2</sub> was stopped and air was introduced into the reactor to burn the remaining hydrogen off the catalyst. The amount of hydrogen which had reacted with CO<sub>2</sub> was calculated by comparing the water produced by the H-reaction to the water produced by the combustion reaction. From these calculations, it was found that 4% of the hydrogen in the coke on the catalyst reacts at 1000°F, while at 1100°F, 10% of the hydrogen in the coke on the catalyst has reacted.

### Conclusions

This report describes an investigation into a novel method to lower the amount of heat produced in the regenerator of an RCC<sup>SM</sup> process unit. Three metal promoters (Cu, Sr and Ba) were found for the Boudouard Reaction which allowed the reaction to occur at 1400°F without severely affecting the cracking activity of the catalyst. Another promising result of this investigation was that a fraction of the hydrogen in coke reacts with CO<sub>2</sub> at 1000°F. At this temperature, a portion of hydrogen could be removed from the catalyst in the reactor stripper, thereby lowering the amount of hydrogen in coke which must be burned off the catalyst. This would allow for the processing of heavier feedstocks in an RCC<sup>SM</sup> process unit, while maintaining moderate temperatures in the regenerator.

### References

1. Zandona, O. J., Busch, L. E., and Hettinger, Jr., W. P., NPRA 80th Annual Meeting, Paper AM-82-61, March 21-23, 1982
2. Boudouard, Ann Chim. Phys., 24 5 (1901).
3. Holstein, W. L., Bodart, M., J. Catal. 75 337 (1982)
4. Jalan, B. P., Rao, Y. K., Carbon 16 175 (1978)
5. Stull, D. R., Westrum, Jr., E. F., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds", John Wiley and Sons, Inc., New York, 1969
6. McKee, D. W., General Electric Technical Information Series, Report No. 78CRD076, Schenectady, NY, April, 1978
7. Hettinger, Jr. W. P., Beck, H. W., Cornelius, E. B., Doolin, P. K., Kmecak, R. A. and Kovach, S. M., Div. Petrol. Chem. Preprints, ACS 28 (4) 920 (1983)
8. Sotirchos, S. V., Mon, E., and Amundson, N. R., Chem. Eng. Sci. 38 55 (1983)
9. Marsh, H. and Rand, B., Carbon 9 63 (1971)
10. Hippo, E., and Walker, Jr., P. L. Fuel 54 245 (1975)

Table 1  
Thermodynamic Parameters

Reaction	H (kcal/mole)		G (kcal/mole) at 1000°K
	at 298°K	at 1000°K	
$C + 1/2 O_2 \rightleftharpoons CO$	-26.42	-26.77	-47.95
$C + O_2 \rightleftharpoons CO_2$	-94.05	-94.32	-94.61
$H_2 + 1/2 O_2 \rightleftharpoons H_2O$	-57.80	-59.24	-46.04
$C + CO_2 \rightleftharpoons 2CO$	+41.21	+40.78	- 1.29
$H_2 + CO_2 \rightleftharpoons H_2O + CO$	+ 9.83	+ 8.31	+ 0.62

Table 2  
Classes of Boudouard Reaction Promoters

<u>High Activity</u>	<u>% Coke Reacted</u>	<u>Low Activity</u>	<u>% Coke Reacted</u>
Li	69	Mo	29
Co	55	Sn	28
CuCl <sub>2</sub>	55	Ca	27
Ni	53	Ti	25
Rh (0.5 wt%)	53	Cr	25
Fe	52	La	25
Na	52	Y	25
Ru (0.5 wt%)	52	Zn	24
Sr	46	Zr	24
Cu(NO <sub>3</sub> ) <sub>2</sub>	42	U	23
		B	22
<u>Moderate Activity</u>		Ba	22
		Cs	22
V	35	K	20
Ag	31	In	20
Bi	30	Mn	20
		Cd	16
		None	15
		W	15
		Sb	9

Catalyst - Super DX w/1.10% C

Temperature - 760°C

Reaction Time - 30 minutes

Promoter Concentration - 1.0 wt% except where noted

Table 3

MAT Results of Promoted Catalysts

<u>Promoter</u>	<u>Concentration (wt%)</u>	<u>Conversion (vol)(%)</u>	<u>CPF</u>	<u>HPF</u>
None	0	61	1.2	13
Li	1.0	10	3.9	10
CuCl <sub>2</sub>	1.0	65	1.5	17
Cu(NO <sub>3</sub> ) <sub>2</sub>	1.0	62	1.6	18
Sr	1.0	50	1.2	10
Ba	1.0	56	1.1	9
Fe	1.0	52	2.3	22
Ni	1.0	53	3.2	33
Li	0.5	16	3.7	11

Table 4

The Effect of Promoter Concentration on the Boudouard Reaction

<u>Li Conc. (wt%)</u>	<u>% Coke Reacted</u>
1.0	69
0.5	44
0.33	35
0.1	25
<u>Rh Conc. (ppm)</u>	
5000	53
500	44
50	26
5	17

Table 5

Sequence of Promoter Addition

<u>Catalyst</u>	<u>%C Reacted</u>	<u>Sequence</u>
1.0 wt% Ba on Catalyst X	.64	Coke over Ba
1.0 wt% Ba on Catalyst X	.71	Ba over Coke
1.0 wt% Ba on Catalyst G	.74	Coke over Ba
1.0 wt% Ba on Catalyst G	.84	Ba over Coke

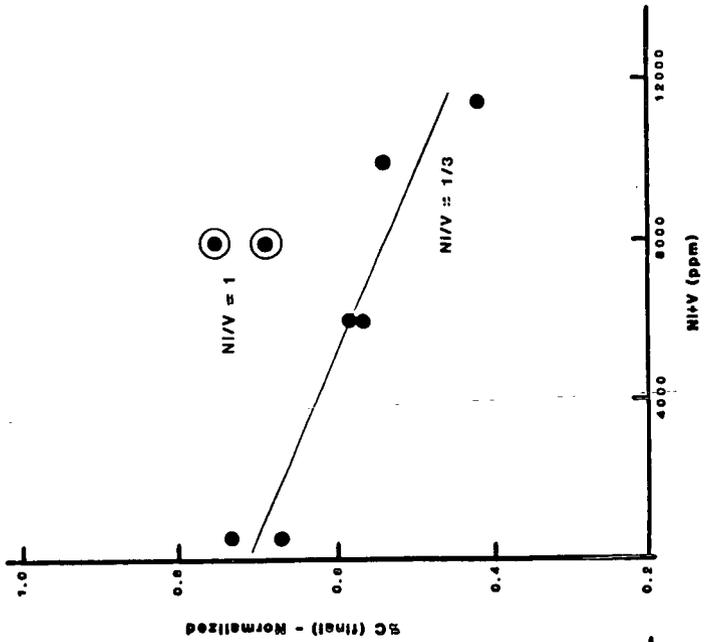


Figure 2. The Effect of Metals on Promoter Activity - Strontium

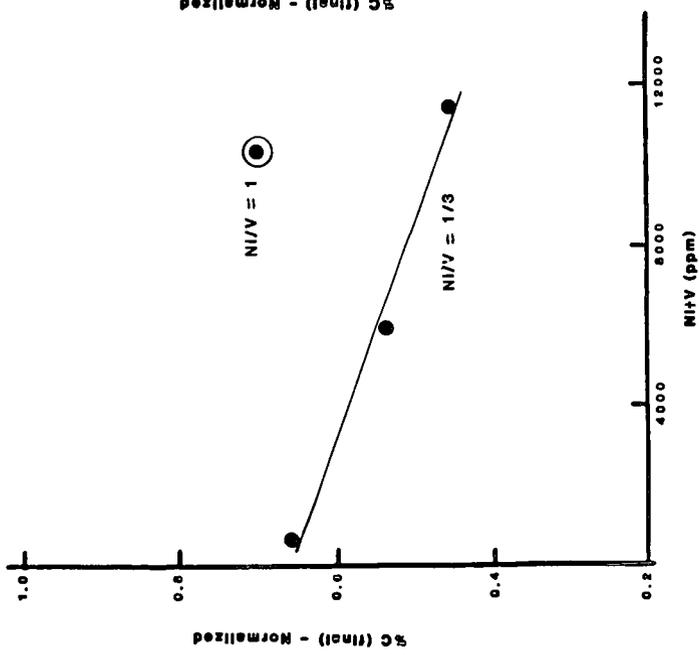


Figure 1. The Effect of Metals on Promoter Activity - Copper

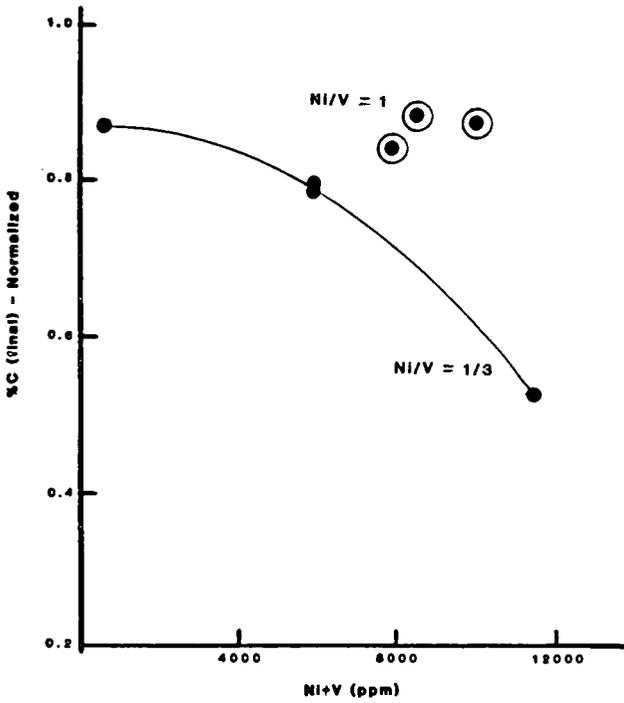


Figure 3. The Effect of Metals on Promoter Activity - Barium

■ MRS Sorbent  
● RCC Catalyst

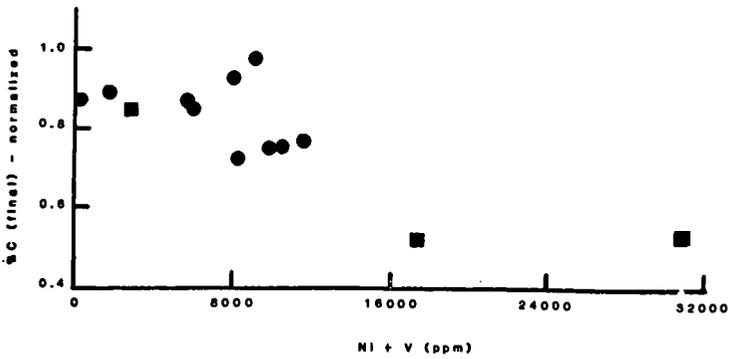


Figure 4. The Effect of Metals on the Rate of the Unpromoted Boudouard Reaction

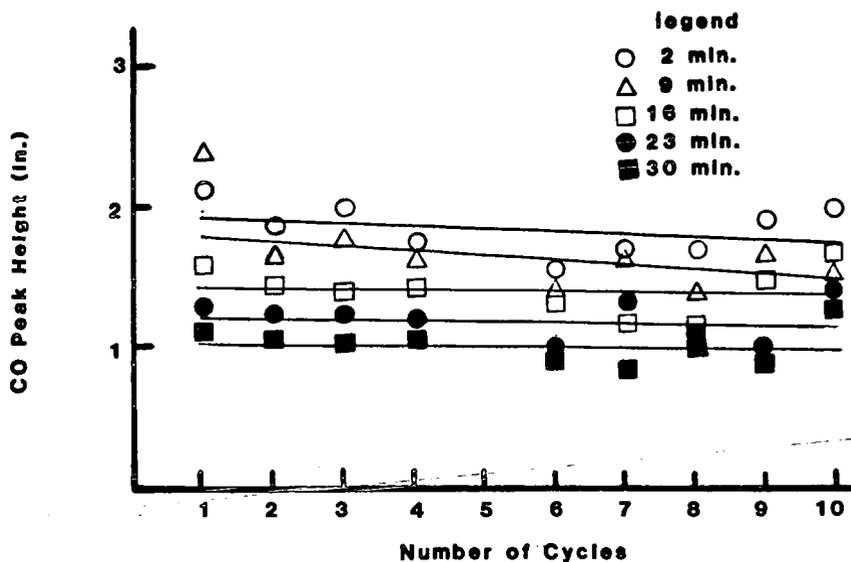


Figure 5. The Effect of Repeated Coking-Regeneration Cycles on the Activity of the Boudouard Reaction Promoter

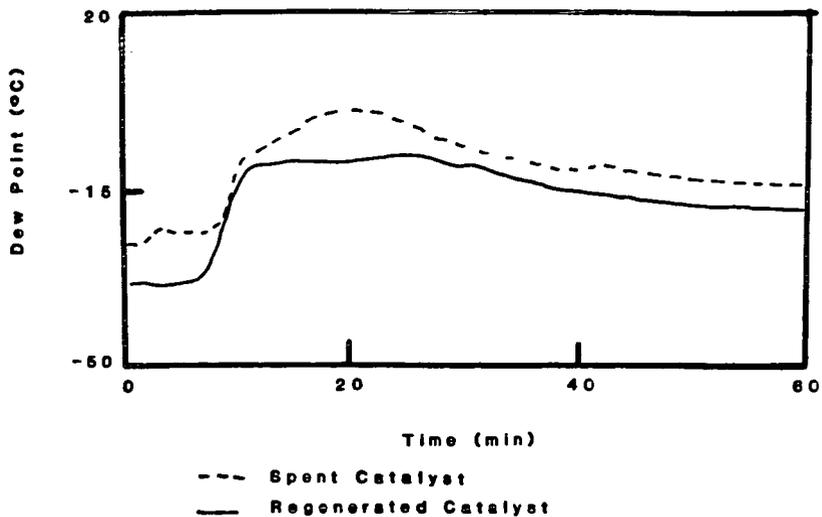


Figure 6. H-Reaction Comparison of Spent and Regenerated Catalysts

HEAT BALANCE IN RCC UNIT  
 FUNCTION OF: CON. CARBON, H<sub>2</sub>O ADD'N, H IN COKE,  
 CO<sub>2</sub>/CO RATIO=1/1

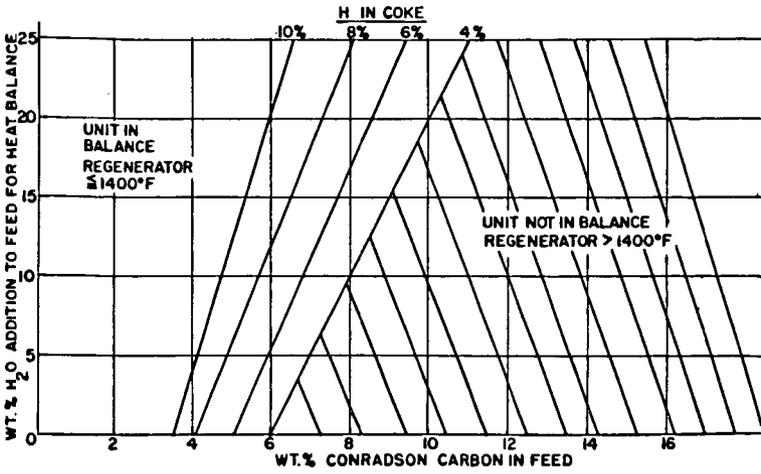


Figure 7. Heat Balance in RCC Unit

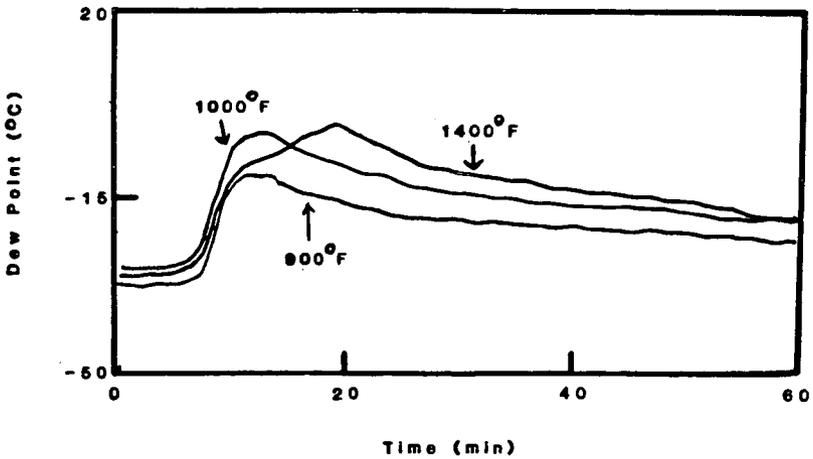


Figure 8. Initiation Temperature of the H-Reaction