

Fluidized Bed Combustion of Petroleum Cokes:  
Kinetics and Catalytic Effects

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INTRODUCTION

In the fluid coking process, large quantities of coke particles are circulated between a burner vessel and the fluid coking reactor, with the coke-to-fresh feed ratio generally about 7 to 8 pounds of coke per pound of residual feed. During each burning cycle, a portion of coke equivalent to about 5% of the charge is burned off, and the hot coke particles are then returned to the coker supplying process heat. As a result of this type of repeated burning and coke deposition cycle, the coke is deposited in multiple, thin "onion-skin" layers. Product coke is withdrawn from the burner vessel, the temperature of which is maintained between  $\sim 595^\circ$  and  $650^\circ\text{C}$ . Because the fluid coking process itself takes place at  $\sim 510^\circ\text{C}$ , followed by the coke being first steam stripped and then burned at  $\sim 625^\circ\text{C}$ , an essentially "dry" coke product is produced, i.e., one which is free of residual oils.

In the delayed coking process, coke is produced in a batch fashion. Residual oil is fed to a coke drum while a companion drum, used in the previous cycle, is de-coked. Product oil vapors pass upward through the forming coke mass en route to exiting. Coke drum inlet temperatures are maintained at  $\sim 485^\circ\text{C}$ - $500^\circ\text{C}$  while the outlet is maintained at  $\sim 440^\circ\text{C}$ ; thus, cooling of the charge takes place during the 24 hour fill cycle. This process, therefore, produces coke at a lower temperature than fluid coking. Hence, the coke product from a delayed coking process is not free of residual oils ( $\sim 2$ - $10$  wt.% on coke).

Although fluid coking is attractive from the viewpoint of higher liquid yield, the coke tends to be higher in sulfur than delayed coke, which could create  $\text{SO}_x$  pollution problems in any subsequent combustion application. In addition to the sulfur question is that of the intrinsic combustibility of fluid coke vs. delayed coke. Since little information is available in the literature on this point, the present work examined whether process differences have any major impact on the combustion characteristics of the coke products.

A second goal of this study was the investigation of the possibility of catalytically enhancing coke burning rates by employing separate particle catalysis. Though the catalytic oxidation effect of metals impregnated on solid carbonaceous fuel has been recognized for many years, no industrial process using this catalytic technique is in operation due to concerns over the cost of catalyst loss and possible environmental effects of emitted metal particles (1). Fluid bed combustion of solid fuels for steam generation operates at temperatures which may be low enough ( $\sim 650$  to  $900^\circ\text{C}$ ) for catalytic effects to be operative. Such catalysis would allow increased throughput for a given unit size or permit the use of a smaller unit for a given steam production rate. Catalytically enhanced combustion of solid fuels such as petroleum cokes by active metals on separate particles could obviate the above cited problems associated with direct impregnation of catalysts on a solid fuel.

## EXPERIMENTAL

Coke samples were first calcined in nitrogen for ~1 hour at a temperature in excess of the highest anticipated experimental temperature (~850°C) to drive off any residual volatiles which might complicate data interpretation. As noted above, little or no volatiles evolution was observed in the case of fluid coke; delayed coke samples did evolve some volatile constituents. The delayed coke samples included both "needle" and "sponge" cokes, which have different morphologies as reflected by their names. Also, in the case of the delayed coke samples, a brief exposure (~90 sec.) to high temperature air was employed to effect a mild surface area enhancement. Thus, all the samples are compared at "dry" conditions (i.e., free of residual oil volatiles) and at similar initial surface areas. Properties of these materials are given in Table 1. At each temperature, repeat runs with successively smaller coke particle sizes were performed until burning rates remained unchanged, thereby insuring that all burning rate data were uninfluenced by diffusion.

The sample of coke to be burned was diluted to 0.1-1.0 wt.% in a bed of acid washed sand particles. The bed was then fluidized in N<sub>2</sub> and brought to reaction temperature in a three zone furnace. Initiation of the experiment, collection of data and termination of the run were all computer controlled. Essentially, the solenoid valve supplying N<sub>2</sub> to the flow controller closes and the O<sub>2</sub> valve opens to start an experiment. Combustion gases leaving the fluid bed are quenched, dried and filtered. An NDIR monitors the CO and CO<sub>2</sub> concentrations and the computer records the CO levels and bed temperature as a function of time. The interval<sup>x</sup> between readings accelerates or decelerates depending upon the CO level in the product gases. Bed isothermality was usually  $\pm 2-3^\circ\text{C}^x$  and the oxygen supply rate was generally  $\geq 10$  times the consumption rate. Experiments were conducted over the temperature range from 500-600°C; reactor pressure was atmospheric.

Preparation of candidate catalytic materials was accomplished by impregnation of clean sand using aqueous solutions containing a quantity of metal sufficient to provide the desired loading (generally ~1 wt.%). The dried preparations were then O<sub>2</sub> calcined at ~800°C prior to use. When Pt preparations were made (using H<sub>2</sub>PtCl<sub>6</sub>), dried samples were H<sub>2</sub> reduced (~2 hours at 425°C) prior to O<sub>2</sub> calcination. A low surface area support (viz. sand) was chosen since solid-solid contacting at the exteriors of the fuel and catalyst particles would be the likely mechanism of any catalytic combustion enhancement; "interior" active sites present in high surface area catalyst formulations would likely be unavailable for catalyzing the primary combustion step (C+O<sub>2</sub>→CO/CO<sub>2</sub>). Metals analyses of catalyst-impregnated sand samples taken from the bed before and after combustion showed that no measurable decrease in catalyst concentration occurred during the course of any of the experiments. In addition, negligibly small amounts of bed material were lost to entrainment.

## RESULTS AND DISCUSSIONS

### Burning Characteristic of Fluid Coke vs. Delayed Coke

The burning rate data for all coke samples tested were adequately described by first order kinetics over ~85% of the burn off. As illustrated in Figure 1, a plot of the natural log of the fraction of unburned carbon vs. time is well-fit by a straight line, the slope of which is the apparent first order rate constant.

Figure 2 is an Arrhenius plot of the rate constant data obtained for the delayed coker needle coke samples; the activation energy is ~41 kcal/mole. This value is in excellent agreement with that reported recently for the combustion of a sample of petroleum coke used in the preparation of pre-baked anodes for aluminum production (2). This value is also comparable to that observed for uncatalyzed combustion of carbon deposited on solid oxide supports (3). Additionally, 41 kcal/mole is in good agreement with the value calculated (4) based on literature data for a wide variety of carbonaceous materials including some delayed coker petroleum cokes. For comprehensive treatments of carbon combustion/ gasification kinetics, the reader is referred to several excellent reviews (5,6,7).

Figure 3 is an Arrhenius plot of the rate constant data for the fluid coke samples. Again, the data define a straight line, the slope of which yields an activation energy of ~27 kcal/mole. This value is in good agreement with ~30 kcal/mole found over a slightly lower temperature range for carbons doped with vanadium at levels roughly equivalent to that of the fluid coke (8). For comparison, Figure 4 shows Arrhenius plots for both delayed coker needle coke and fluid coke, as well as points obtained for sponge coke, which is a delayed coke with substantially larger metals content than the needle coke samples. The lines in Figure 4 converge at ~550°C, showing behavior very consistent with that found for pure and vanadium-doped carbon oxidation (8). This convergence indicates the increasing influence of the higher activation energy, thermal oxidation relative to the catalyzed oxidation reaction.

Figure 4 shows that fluid coke burns at a somewhat faster rate than delayed coker needle coke at temperatures below ~550°C. However, delayed coker sponge coke behaves in a manner similar to fluid coke. Both of these materials have high metals contents (Table I) relative to delayed coker needle coke, which exhibits lower rates and a higher activation energy. Thus, it is probable that petroleum cokes having higher metals concentration exhibit catalytically influenced combustion. In fact, such catalytic effects were reported (8) for carbons containing as little as 150 ppm vanadium, with little change in activation energy for vanadium concentrations up to 3.5%!

In summary, it appears that process origin does not have a major impact on the burning rates of "dry" petroleum cokes having similar initial surface areas and metals contents. The metals content of the coke can exert a catalytic influence on its burning rate. However, this effect is lessened at higher temperatures. Based upon these observations, it was inferred that any major differences between the combustibility of fluid coke and delayed coke under practical industrial conditions would likely be due to the presence of the heavy residual oils in the delayed coke. Volatilized residual oils would be more readily oxidized than the delayed coke itself and thus would aid in initiating and stabilizing the coke combustion process.

#### Enhancement of Coke Burning Rates by Separate Particle Catalysis

Effect of temperature Burning rate data for needle coke burned in the presence of clean sand and sand impregnated with metallic catalysts are presented in Figure 5. It is apparent that all the candidate catalytic materials investigated produced a burning rate enhancement. The apparent activation energy for coke burning in a 1% Pt/sand bed was ~17 kcal/mole versus ~41 kcal/mole for the baseline

(clean sand) data. The divergence of the two lines shows that the relative rate enhancement decreases with increasing temperature. When extrapolated, the two lines converge at a point corresponding to  $\sim 555^{\circ}\text{C}$ , virtually identical to the point of convergence observed for the burning rate data presented in Figure 4 which showed the effect of metals intrinsic to the coke. This consistent finding suggests that a significant catalytic benefit of metals (whether intrinsic or present on separate particles) for burning rate enhancements may be realized only at temperatures below  $\sim 550^{\circ}\text{C}$ . Furthermore, the data indicate that this effect is not highly sensitive to the identity of the metal.

Choosing  $505^{\circ}\text{C}$  as a comparison temperature, the data show that both 0.1% Pt and 1% Pt are equally effective, increasing the rate by a factor of 2.2. This behavior might be expected on such a low surface area support since more than enough Pt is present in both cases to cover the available surface. Also, nickel oxide is as effective as Pt in enhancing the burning rate, while cobalt oxide is only slightly inferior. Both Ni and Co have been previously reported as having catalytic activity for carbon gasification when directly impregnated on the solid fuel (9). As shown in Figure 5, sodium oxide is also quite effective as a catalyst. Alkali metal oxides have also been identified previously as effective gasification catalysts when impregnated on the fuel (10,11). However, they are believed to function by a different mechanism than noble or transition metals (12), some evidence of which is given below.

The data in Table II present the  $\text{CO}/\text{CO}_2$  ratio in the combustion gases at 50% carbon burnoff. In all baseline cases with clean sand as the bed material, both CO and  $\text{CO}_2$  were produced over the course of the burn in fairly fixed proportions, while in all Pt and transition metal experiments CO was never observed, indicating more efficient combustion. The similarity between the  $\text{CO}/\text{CO}_2$  ratios of the baseline data and the sodium oxide data indicates that the alkali metal oxide enhances gasification of carbon to CO but does not effectively improve combustion efficiency by promoting complete conversion of CO to  $\text{CO}_2$ .

Figure 6 presents baseline and catalytic results obtained using sponge coke. Catalysis was again observed, but the 40% rate enhancements at  $500\text{--}510^{\circ}\text{C}$  are more modest than those observed with needle coke. The similar behavior of fresh and used Pt suggest that there is no rapid deterioration in performance. In contrast, fresh nickel oxide, which was initially as effective as Pt, rapidly lost its activity as shown by a decrease in burning rate and the appearance of CO in the combustion gases upon subsequent use. Though this suggests that the catalyst was being poisoned, presumably by coke-derived impurities, it is not clear why, under similar circumstances, the Pt activity remained unaffected. For comparison, Figure 7 shows baseline and 1% Pt/sand catalytic data for fluid coke. At  $\sim 505\text{--}510^{\circ}\text{C}$  a moderate rate enhancement of  $\sim 50\%$  was observed.

Based on the collective results shown in Figures 5-7, it may be concluded that no significant rate enhancement benefits are to be gained by separate particle catalysis in practical fluid bed combustors, which typically operate at temperatures  $>650^{\circ}\text{C}$ . However, the results given in Table II show that separate particle catalysis can be beneficial in completing the conversion of CO to  $\text{CO}_2$ , resulting in higher combustion efficiencies and minimizing CO emissions from the unit. This benefit of lowered CO emissions, even

at the higher temperatures typical of practical fluid bed combustors, is not unexpected in light of the proven effectiveness of Pt CO combustion promoter additives used in the fluid bed, air regeneration of fluid cracking catalysts at temperatures  $>650^{\circ}\text{C}$  (13).

Effect of intrinsic metals The higher rate increases observed with low-metals needle coke vs. sponge and fluid cokes parallel the relative burning rates discussed above in the absence of separate catalytic particles. Moreover, this behavior suggests that the extent to which a rate enhancement can be obtained with separate particle catalysts also depends upon the intrinsic metals content of the coke. To examine this point further, some additional data were obtained by burning toluene-derived soot (96% C, 2% O, 2% H) as a convenient model of a metals-free carbonaceous pyrolysis residue.

Although differing in "process" origin, both coke and soot are carbonaceous pyrolysis products having quite similar elemental analyses. Furthermore, both coke and soot have been shown elsewhere to have very similar reactivities and activation energies ( $\sim 39$  kcal/mole) with respect to combustion (4). In contrast, high purity graphite does not exhibit burning behavior similar to that of low-metals needle coke, as evidenced in related studies where the burning rate constant for ultra-high purity graphite ( $< 5$  ppm total impurities) was found to be over two orders of magnitude lower than that of the coke. This result is also consistent with earlier work which showed that high purity graphite has a reactivity  $\sim 3$  orders of magnitude lower than coke and has a much higher activation energy ( $\sim 50$  to  $70$  kcal/mole) (4). This evidence shows that soot better models "high purity" petroleum coke burning behavior than do other carbonaceous residues such as ultra-high purity graphite.

Soot experiments were performed over clean sand, over 1% Pt/sand, and over clean sand with the soot directly impregnated with 1% Pt. These results are summarized in Table III. Despite its extremely fine particle size, in the absence of catalyst particles, the soot burning rate constant at  $505^{\circ}\text{C}$  was 6-7 times lower than that of low-metals needle coke. This factor seems reasonable in light of the soot's zero metals content and the discussions in the previous section.

In discussing the impact of added catalyst particles, the use of burning rate enhancements, i.e. relative burning rates with and without a catalyst, will facilitate comparisons among the various carbonaceous materials. Figure 8 shows the relative burning rates ( $k_{\text{catalyst}}/k_{\text{baseline}}$ ) at  $\sim 505^{\circ}\text{C}$  for soot and all the cokes investigated using 1% Pt on sand. The data point for needle coke is plotted somewhat arbitrarily at 30 ppm since the reported analytical results provided only upper bounds on the Ni and V contents (see Table I). The plot indicates that the extent of rate enhancement obtained by separate particle catalysis is a function of the intrinsic metals content of the solid fuel being burned. Therefore, above a certain threshold concentration of metal ( $\sim 100$  ppm Ni + V) intrinsic to the carbonaceous fuel, the otherwise large influence of external catalysts will be greatly diminished.

Pertinent to the question of intimacy between the metal and the solid fuel, a 17 fold increase in rate was obtained by separate particle catalysis of metals-free soot (Table III). In this case, soot was burned in a bed of Pt impregnated sand where the initial atomic Pt/C ratio was  $\sim 0.26/1$ . A 30 fold increase resulted, however,

when soot impregnated with 1 wt.% Pt was burned in a bed of clean sand where the initial atomic Pt/C ratio was 400 times lower. Clearly, the more intimate the contact between carbon and metal, the more effective the catalysis.

Mechanistic implications The fact that coke burning rate enhancements are observed when the bed material (sand) is impregnated with metals indicates that "solid-solid" catalytic interactions are occurring between the coke particles and bed particles in the presence of oxygen. Regardless of the particular metal or metal oxide particle, intimate contact between it and the carbon surface is required for the oxidation-reduction cycle of the metal particle to occur at the carbon surface, which is the generally accepted mechanism for the catalyzed oxidation of carbon (12). It is highly unlikely that gas phase transport of the metal or metal oxide to the carbon surface is involved under the current experimental conditions due to the low vapor pressures of these species at temperatures below 550°C.

The first step in any heterogeneous catalytic reaction is the transport of reactants from the bulk phase to the external surface of the catalyst. In the present work, only the external mass transfer step can influence and mask the intrinsic kinetics since the catalyst particles employed are non-porous and intraparticle diffusion is not a factor. If the external mass transfer step is rate controlling, then the observed apparent activation energy will be lower than that of the true activation energy of the catalyzed chemical reaction. This results because, compared to the reaction rate constant, the mass transfer coefficient is much less sensitive to changing temperature.

Standard methods exist for estimating the importance of external mass transfer gradients on the observed kinetic parameters (14). However, those procedures were developed for fluid phase reactants and, therefore, are not directly applicable to the case at hand where the reactants are macro-sized carbon particles. Nevertheless, the strong influence of convective transport of coke particles to the active external surface seems reasonable in light of the size of the solid reactants. Such an influence would explain the decline in apparent activation energy from ~27 kcal/mole for carbon particles containing a significant amount of intimate catalytic sites (fluid and sponge cokes) to ~17 kcal/mole where few such sites exist and transport of the carbon particle to external catalytic centers is required (needle coke). External mass transport rate control would also account for the apparent insensitivity of catalyst type on the extent of the rate enhancement observed for needle coke burning in the presence of external catalyst particles versus burning in the absence of an external catalyst.

#### CONCLUSIONS

The burning rates of "dry" petroleum cokes (i.e., cokes which are free of residual oil volatiles) having similar initial surface areas are not influenced by process origin (delayed vs. fluid coking). Differences in burning rate among the coke samples tested are related to the metals level in the coke which can exert a catalytic influence on the burning rate. This effect diminishes with increasing temperature as higher activation energy thermal reactions begin to dominate.

The addition of separate particles of low surface area catalytic solids can accelerate the combustion of petroleum coke and similar carbonaceous residues. The extent of the rate enhancement from an external catalyst declines with increasing temperature and increasing intrinsic metals content of the solid fuel. Moreover, these findings suggest that the primary benefit from separate particle catalysis in practical fluid bed combustors for steam generation would be enhanced conversion of CO to CO<sub>2</sub>. Finally, the low activation energies observed are qualitatively consistent with a rate-limiting step involving transport of coke particles to the surface of the catalyst particles.

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TABLE I

COKE ANALYSES

	<u>Needle Coke+</u>	<u>Sponge Coke+</u>	<u>Fluid Coke*</u>
C (wt%)	93.8	90.4	87.3
H	2.4	1.7	1.6
O	2.3	1.7	1.6
N	0.48	1.1	1.2
S	0.54	3.68	8.0
Ash	0.53	1.17	.33
Ni (ppm)	<20	145	275
V	<25	390	540
Cu	5	7	5
Fe	200	215	60
Surface Area, m <sup>2</sup> /g	8	6	8

+ N<sub>2</sub> Calcined to 650°C, air burned at 650°C, ~90 sec, ~1hr.  
N<sub>2</sub> calcination at 600°C.

\* ~1 hr. N<sub>2</sub> calcination at 600°C.

TABLE II

CO/CO<sub>2</sub> RATIO AT 50% NEEDLE COKE BURN-OFF (505°C)

<u>Catalyst</u>	<u>CO/CO<sub>2</sub></u>
None	0.64
.1% Pt	0
1% Pt	0
1% NiO	0
1% CoO	0
1% NaO	0.67

TABLE III

INFLUENCE OF Pt ON TOLUENE SOOT BURNING RATE AT 505°C

	<u>k (min<sup>-1</sup>)</u>	<u>k<sub>Pt</sub>/k<sub>base</sub></u>
Base case (no catalyst)	0.015	1.0
1 wt% Pt on Sand	0.260	17.3
1 wt% Pt on Soot	0.452	30.1

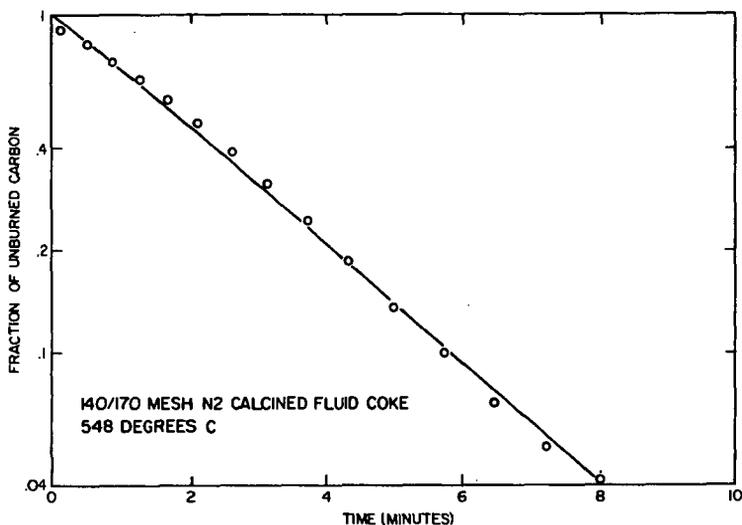


FIGURE 1. FRACTION OF UNBURNED CARBON VS. TIME

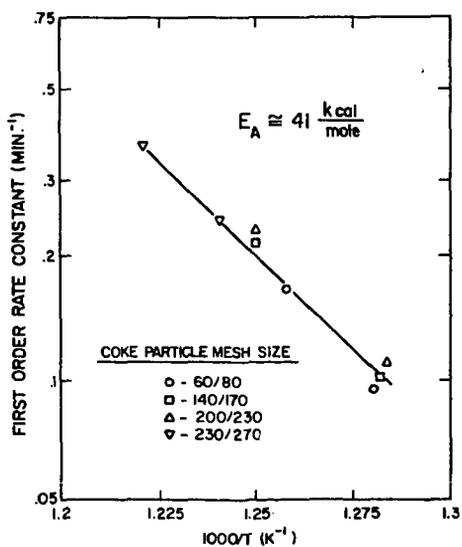


Figure 2. ARRHENIUS PLOT FOR NEEDLE COKE COMBUSTION

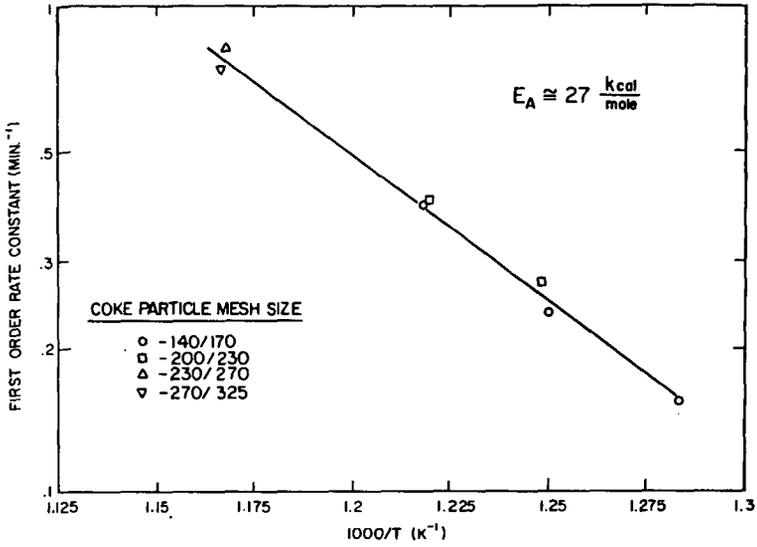


Figure 3. ARRHENIUS PLOT FOR FLUID COKE COMBUSTION

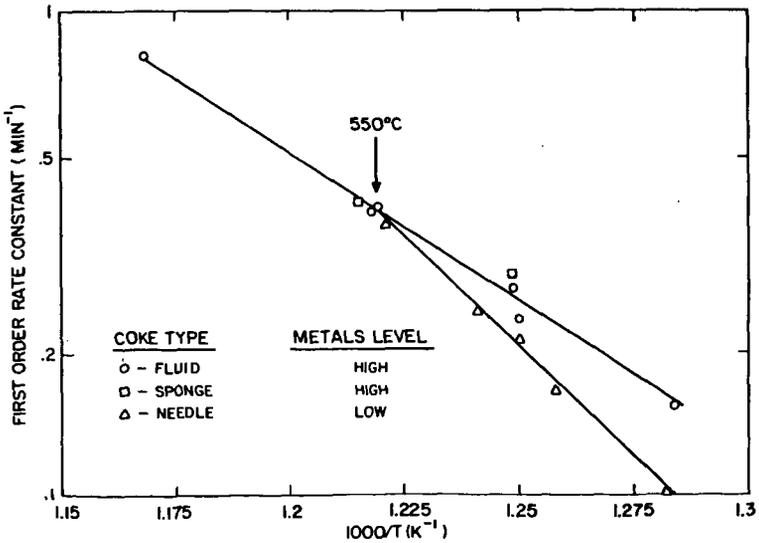


Figure 4. INFLUENCE OF COKE METALS CONTENT ON ARRHENIUS BEHAVIOR

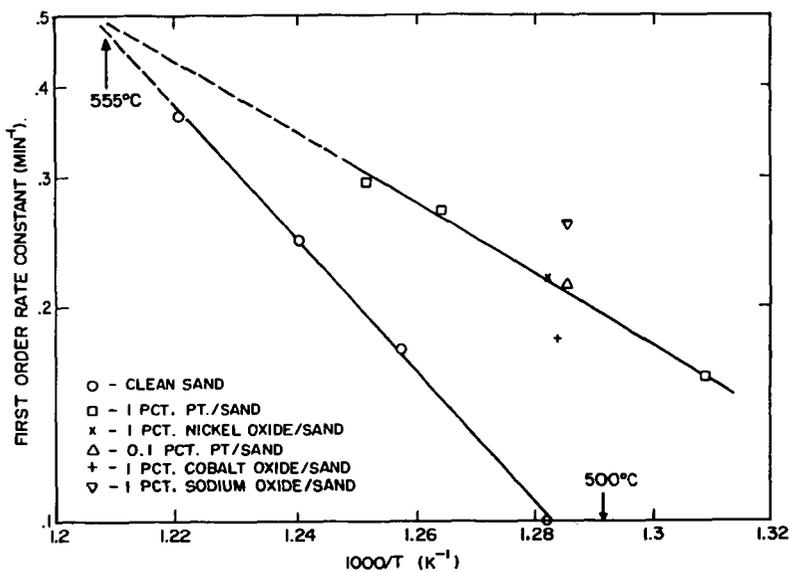


Figure 5. ARRHENIUS PLOT FOR NEEDLE COKE COMBUSTION: EFFECT OF SEPARATE PARTICLE CATALYSIS

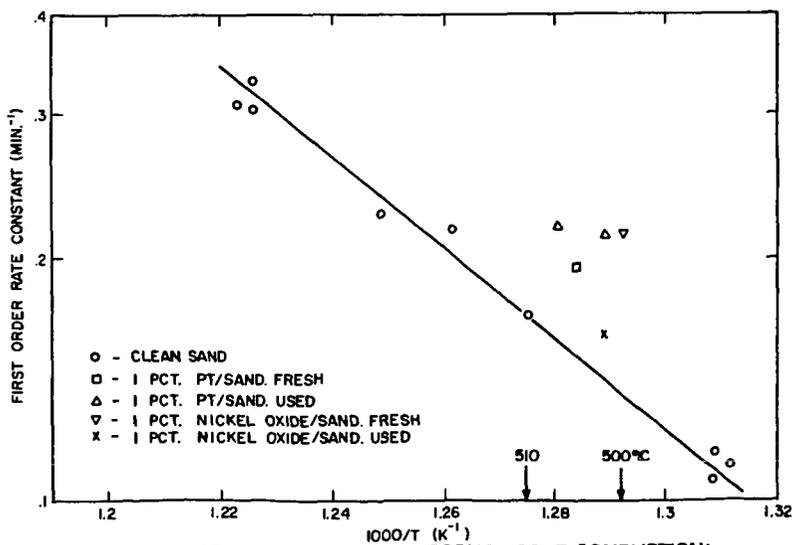


Figure 6. ARRHENIUS PLOT FOR SPONGE COKE COMBUSTION: EFFECT OF SEPARATE PARTICLE CATALYSIS

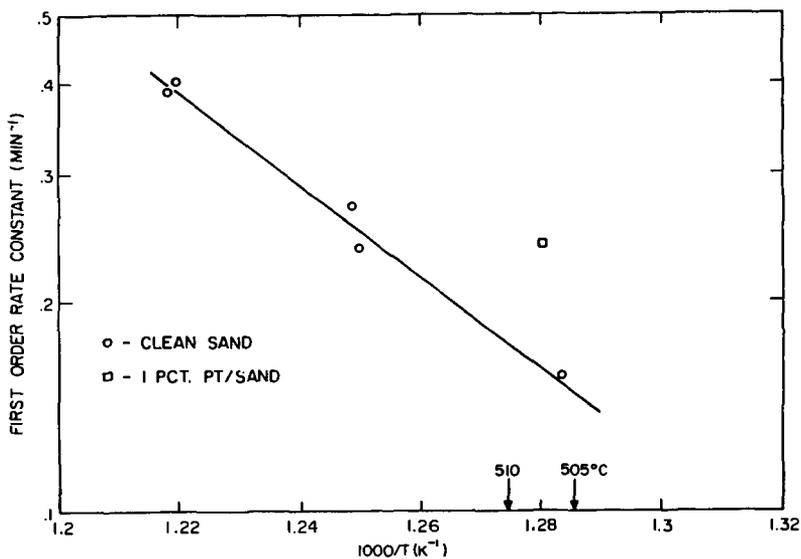


Figure 7. ARRHENIUS PLOT FOR FLUID COKE COMBUSTION: EFFECT OF SEPARATE PARTICLE CATALYSIS

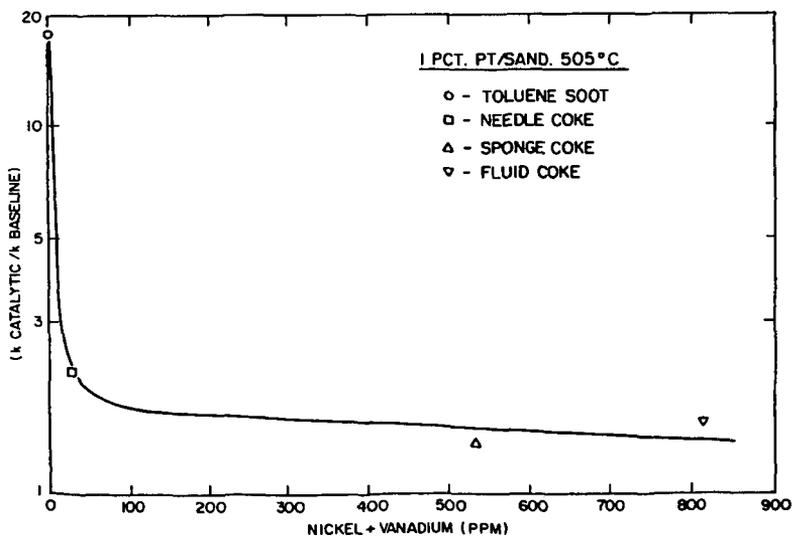


Figure 8. RATE CONSTANT RATIO VS. INTRINSIC METALS CONTENT