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Part 1:
Kinetics of the Causticization Reaction

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Black Liquor Gasification with Direct Causticization Using Titanates in a Pressurized Entrained-Flow Reactor, Part 1: Kinetics of the Causticization Reaction

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The convective heat transfer coefficient is calculated by using heat transfer correlations for a sphere in gas flow. The viscosity and thermal conductivity of the fluid used in the heat transfer correlations are estimated by using conventional methods [17]. More details concerning the physical and chemical data used in the model can be found in the Appendix.

The kinetic models used in this study are the Valensi-Carter model, the phase boundary reaction model, based on spherical geometry, and a "modified shrinking-core model" (see Table I). In the modified shrinking-core model, the product growth is influenced by both diffusion and first-order reaction and assumes a sphere reacting from the surface inwards. The change of the total radius is taken into account by using the ratio z, as in the Valensi-Carter model.

TABLE I
MODELS USED TO DESCRIBE SOLID STATE REACTIONS, WHERE k IS THE RATE CONSTANT, t THE TIME, z THE VOLUME OF PRODUCT FORMED PER VOLUME OF REACTANT CONSUMED, r THE RADIUS, AND r_0 THE INITIAL RADIUS OF THE SPHERE

MODEL	RATE-CONTROLLING STEP	EQUATION (DIFFERENTIAL FORM)
Valensi-Carter, [18]	Diffusion	$\dfrac{dr}{dt} = -k_1\left(r - \dfrac{r^2}{\left(zr_0^3 + r^3(1-z)\right)^{1/3}}\right)^{-1}$
Phase-boundary spherical geometry, [19]	Phase-boundary reaction	$\dfrac{dr}{dt} = -k_2$
The "modified shrinking-core model," [20]	Diffusion and first-order reaction	$\dfrac{dr}{dt} = -\left(\dfrac{1}{k_3} + \dfrac{1}{k_4}\left(r - \dfrac{r^2}{\left(zr_0^3 + r^3(1-z)\right)^{1/3}}\right)\right)^{-1}$

Note: k is the rate constant in all cases but it has different units in the different rate models.

In order to take into account the temperature dependence of the reaction rate constants, the Arrhenius equation is used:

$$k = A \cdot e^{-E/RT} \tag{4}$$

where E is the activation energy (J/mol), A is the pre-exponential factor (m²/s or m/s), k is the reaction rate constant (m²/s or m/s), T is the temperature (K), and R is the gas constant (8.3145 J/mol,K). The Arrhenius parameters determined by Nohlgren et al. [13, 21] have been used and extrapolated to the higher temperatures used in this study. For a more detailed description of the models, see Nohlgren [20].
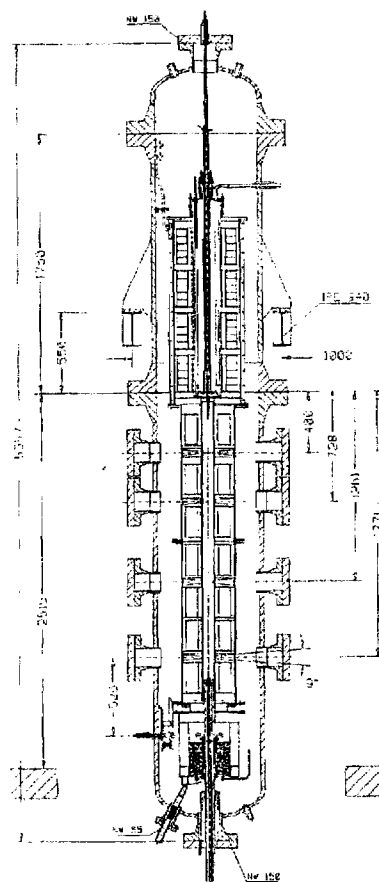
EXPERIMENTAL
Sample Preparation
The reference material (i.e., a sodium carbonate and sodium tri-titanate mixture) was prepared by dissolving sodium carbonate (p.a.) in distilled water and then adding sodium tri-titanate (99%). The suspension was heated to its boiling point to evaporate the water while being stirred with a magnetic stirrer. When the concentration of solids in the suspension had increased sufficiently, the sample was put in a furnace (105°C) to dry overnight. Finally, the dried sample was ground to a fine powder. The powder was sieved and only the size fraction below 38 μm was used. The molar ratio used was $Na_2O \cdot 3TiO_2/Na_2CO_3$ = 5/7 in all of the experiments, which corresponds to the stoichiometric ratio.

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The black liquor and sodium tri-titanate mixture was prepared by mixing stoichiometric amounts of sodium tri-titanate into a 50% dry solids black liquor solution. The stoichiometric amounts of sodium tri-titanate were determined based on the Na_2O and K_2O contents in the black liquor, which were assumed to be equal to Na_2CO_3 and K_2CO_3, and the reaction was assumed to proceed as Reaction (2). The prepared mixture was dried in a furnace (105°C) and ground to a fine powder. The powder was sieved and only the size fraction below 38 μm was used.

Equipment

The pressurized entrained-flow reactor (PEFR) located at the Institute of Paper Science and Technology, Atlanta, USA, is shown in Fig. 2. It consists of a conventional, laminar, entrained-flow reactor inside a pressure shell rated to 8 MPa. Dried and sieved solids (black liquor mixed with sodium tri-titanate or sodium carbonate mixed with sodium tri-titanate) are fed into the reactor using a screw feeder housed in a separate vessel above the reactor and gas preheater. The solid particles are carried into the reaction zone through a cooled feed tube, entrained in a small fraction of the total amount of gas entering the reactor. The bulk of the gas is preheated and enters as a secondary flow, passing through a flow straightener.

Fig. 2. The pressurized entrained-flow reactor. Dimensions are in millimeters

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The particles are heated rapidly to the temperature of the reaction zone and pass through it as they react. At the bottom of the reaction zone, the gases and particles enter a liquid-cooled nitrogen-quenching collector probe where very rapid cooling takes place. High-temperature reactions are effectively stopped in progress. Residence times from about 0.5 to 10 seconds can be obtained by either adjusting the gas velocity or changing the reaction zone length by moving the collector probe.

Conditions and Analyses

The experiments were carried out at three different temperatures (900, 950, and 1000°C), two different pressures (0.5 and 1 MPa), two different gas atmospheres (pure N_2 and 2% CO_2 in N_2), and for two sample mixtures (sodium tri-titanate mixed with either black liquor or sodium carbonate) (see Table II). The average gas velocity was set to 0.30 m/s at 0.5 MPa and 0.20 m/s at 1 MPa. The average feed rate for the reference material was 33 mg/s and, for the black liquor material, 50 mg/s.

TABLE II
EXPERIMENTAL CONDITIONS

Pressure	Temperature		
	900°C	950°C	1000°C
0.5 MPa	N_2 (ref.)	N_2 (ref.)	N_2 (ref.)
	N_2 (bls)	N_2 (bls)	N_2 (bls)
	2 % CO_2 (bls)	2 % CO_2 (bls)	2 % CO_2 (ref.)
			2 % CO_2 (bls)
1 MPa	N_2 (ref.)	N_2 (ref.)	N_2 (ref.)
	N_2 (bls)	N_2 (bls)	N_2 (bls)
			2 % CO_2 (bls)

Notes: ref. = reference material (sodium carbonate and sodium tri-titanate)
bls = black liquor material (black liquor and sodium tri-titanate)

The gas concentration of carbon dioxide at different positions in the PEFR was analyzed on-line by a FT-IR spectrometer. The solid samples collected from the runs were leached and the caustic formed was determined by titration with HCl. A detailed description of the leaching procedure can be found elsewhere [22]. The carbonate content in the leachate was analyzed by gas chromatography (GC). In addition, the amount of Ti in the solid sample was analyzed by x-ray fluorescence (XRF) for the reference material and inductive coupled plasma (ICP) for the black liquor material. All the analyses on the solid sample can be seen in Fig. 3.
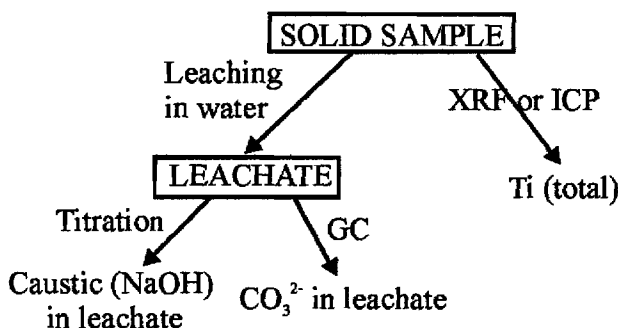

Fig. 3. Schematic diagram of the analyses of the solid material.

RESULTS AND DISCUSSION

Calculation of the Conversion

When sodium tri-titanate reacts with sodium carbonate, sodium penta-titanate is formed via Reaction (2), which forms sodium hydroxide when leached with water via Reaction (3). Therefore, one measurement of the conversion of Reaction (2) is to determine the sodium hydroxide concentration in the solution by titration with HCl. However, in accordance with earlier findings [23], it was found that the sodium tri-titanate also forms substantial amounts of sodium hydroxide, probably by reacting to sodium hexa-titanate via Reaction (5).

$$2\ (Na_2O \cdot 3TiO_2)\ (s) + H_2O \ \leftrightarrow\ 2\ NaOH\ (aq) + (Na_2O \cdot 6TiO_2)\ (s) \tag{5}$$
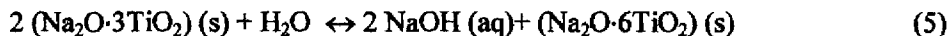
Experimental results from leaching the pure sodium tri-titanate showed that 57 mg of NaOH is formed per gram sodium tri-titanate, which means that 43% by weight of the sodium tri-titanate reacts to form NaOH and sodium hexa-titanate, according to Reaction (5). The sodium hexa-titanate reacts in the gasifier to form sodium tri-titanate:

$$Na_2O \cdot 6TiO_2\ (s) + Na_2CO_3\ (s,l) \ \leftrightarrow\ 2\ (Na_2O \cdot 3TiO_2)\ (s) + CO_2\ (g) \tag{6}$$

The fact that sodium tri-titanate also forms caustic is an advantage in the titanate process since it means that more caustic is produced per gram titanate, i.e. higher caustic concentrations can be obtained. However, it has not yet been studied whether or not the formation of caustic from sodium tri-titanate is concentration dependent. In addition to the formation of caustic from sodium tri-titanate, the black liquor also contains some sodium hydroxide from the beginning. Furthermore, Wåg et al. [24] showed that the structure of black liquor char contains a phenolic-ring system with free carbon sites and catalytic organo-sodium moieties. This structure would, upon leaching in water, form NaOH and Na_2CO_3. Consequently, the black liquor char can also form caustic upon leaching.

In this study, the conversion of sodium tri-titanate and sodium carbonate according to Reaction (2) is the focus, (i.e., the caustic formed from sodium penta-titanate, not the total amount of caustic formation). Therefore, the conversion has been calculated as:

$$x = \frac{caustic\ formed\ in\ the\ sample/g\ Ti - caustic\ formed\ from\ NT_3\ and\ BLS/g\ Ti}{theoretical\ maximum\ caustic\ formed\ /g\ Ti - caustic\ formed\ from\ NT_3\ and\ BLS\ /g\ Ti}$$

where NT_3 = sodium tri-titanate and BLS = black liquor solids.

All of the factors in the conversion expression are presented as g per g titanium, since titanium is the only species constant throughout the reaction, (i.e., some of the organic material in the black liquor is pyrolyzed or gasified). It is difficult to determine the exact amount of sodium hydroxide formed from the black liquor in each sample, since it might change during the reaction. The value used in the conversion calculations is the sodium hydroxide measured in the black liquor from the beginning. Another method of determining the conversion is to use the carbonate concentration in the leachate. However, this was found not to work so well; the explanation is probably that carbonate is first produced and then destroyed during pyrolysis and gasification of black liquor [25]. This makes the carbonate content not only dependent on the progress of Reaction (2), but also on the pyrolysis or gasification of the black liquor. Although the conversion based on the formed caustic presented above has some uncertainties, it was found to be the best method for the black liquor material. When the reference material is used, the conversion can also be calculated from the release of carbon dioxide formed during Reaction (2). However, this method is not suitable for black liquor since the organic carbon also forms carbon dioxide.

Experimental Results and Discussion

Figures 4 to 7 show some examples of the experimental results for the conversion. The conversion for the reference material is calculated based on the release of carbon dioxide and the conversion for the black liquor material is calculated based on the formed caustic discussed above. It can be seen that, for the experiments at 1000°C and 1 MPa, the conversion is above 1, (i.e., impossible). The explanation for this is probably in the assumption that the black liquor forms equal amounts of sodium hydroxide both after and before pyrolysis or gasification. Figure 4 shows an example of a comparison between the results for the reference material and black liquor material. It can be seen that the reaction is much faster for the black liquor material compared to the reference material, which was seen for all of the conditions studied. This is probably due to the sodium carbonate being more distributed in black liquor; this leads to a larger effective contact area between the sodium carbonate and the sodium tri-titanate in the black liquor material compared to the reference material, where the contact probably is more point-to-point between the particles.
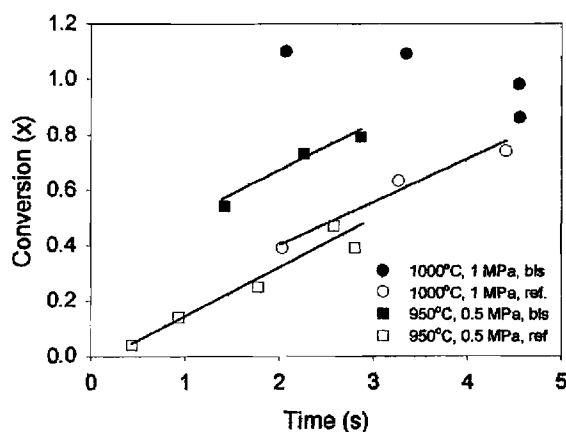

Fig. 4. Comparison between runs with reference material and black liquor material.
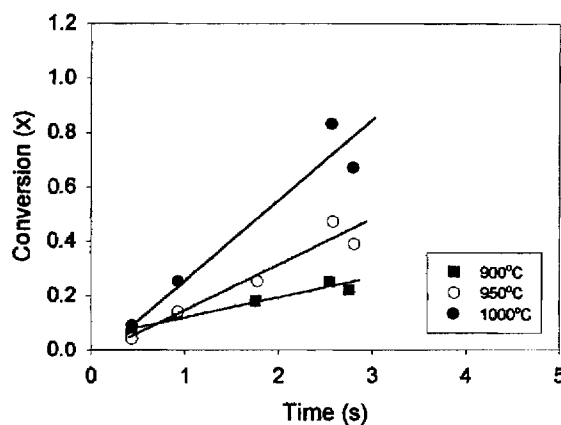

Fig. 5. Comparison between runs in N_2 atmosphere at 0.5 MPa with reference material at different temperatures.
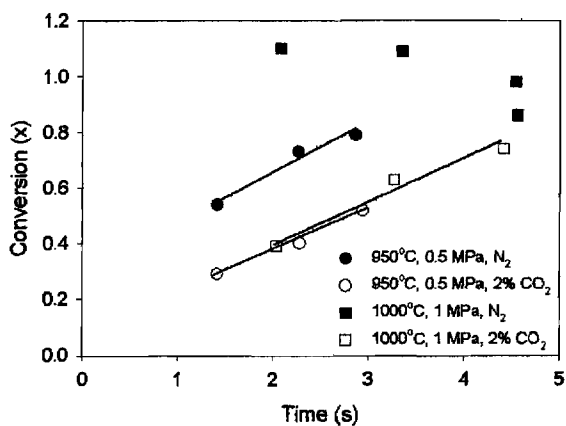

Fig. 6. Comparison between runs in nitrogen atmosphere and runs in 2% carbon dioxide atmosphere.
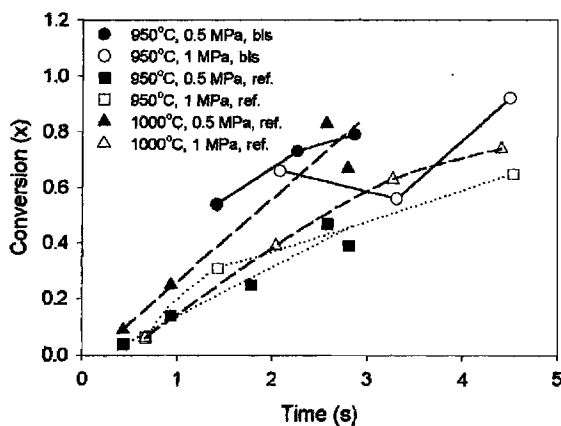

Fig. 7. Comparison between runs at 0.5 MPa and 1 MPa.

Figure 5 shows a comparison between the three temperatures studied (900, 950 and 1000°C) for runs in nitrogen atmosphere at 0.5 MPa with the reference material. The reaction rate increases considerably as the temperature increases, which is consistent with earlier findings at lower temperatures [13]. Consequently, the reaction rate is strongly influenced by the reaction temperature. Figure 6 shows an example of a comparison between runs in nitrogen atmosphere and 2% carbon dioxide atmosphere. The presence of carbon dioxide was found to slow down the reaction, which is consistent with earlier findings [21]. Finally, no clear influence of the pressure has been seen (Fig. 7).

Modeling Results and Discussion

As discussed above, three different kinetic models, the Valensi-Carter, phase boundary, and the modified shrinking-core model, were used to model the conversion degree. The particles are assumed to be spherical, consisting of small grains clogged together as larger agglomerates. In all the models, an initial grain radius of 0.74 µm and an agglomerate radius of 38 µm have been used. The grain radius is the radius used for the mass transfer in the kinetic models, while the agglomerate radius is used in the heat transfer equations. The grain radius is estimated by assuming spherical particles and using the BET specific surface area (1.19 g/m^2) and the density for the sodium tri-titanate material (3400 kg/m^3).

When the modeling results and experimental results are compared, the reaction time (which is based on the particle velocities in the reactor) is important. The particle velocity was calculated from the gas flow entering the reactor based on a laminar flow profile, assuming that the particle velocity is equal to the gas velocity and that the particles stay in the middle of the flow profile, (i.e., the maximum velocity in the laminar flow profile).

Figures 8a and 8b show examples of comparisons between experimental results and the models for experiments in N$_2$ atmosphere and 2% CO$_2$, respectively. It can be seen that all of the experimental results are much faster than predicted by the models, both for the reference material and the black liquor. However, since the reference material reacts more slowly than the black liquor material, there is a smaller difference between the experimental results for the reference material and the models. The difference between the experimental results and the models is probably due to the reaction constants in the models, which are extrapolated from experiments at temperatures of 800-880°C, which are near
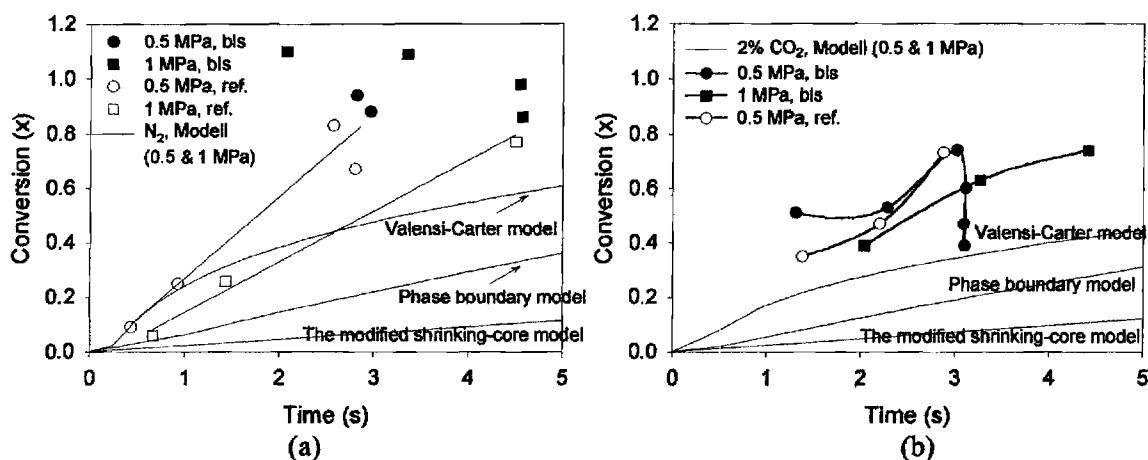

Fig. 8. Comparison between experimental results and the models at 1000°C in
(a) N$_2$ atmosphere (b) 2% CO$_2$ atmosphere.

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the melting point of sodium carbonate (858°C). The temperatures in this work are 900-1000°C, so there is a liquid phase and hence faster kinetics. Furthermore, the temperatures are also much closer to the melting point of sodium penta-titanate (1030°C) and sodium tri-titanate (1130°C). The change between solid and liquid phases, and the fact that the temperature is much closer to the melting point of the sodium titanates, might give rise to other mechanisms that could determine the overall reaction rate, since the mobility of the material increases when the solids approach the liquid phase.

In addition to the difference between the models and the experimental results, it could also be seen that the models showed the same results at 0.5 MPa as at 1 MPa. In the kinetic models, there is no pressure influence; the pressure only influences the heat transfer rate. Consequently, in this case, the heat transfer is faster than the mass transfer.

CONCLUSIONS

The experimental results showed that the formation of sodium penta-titanate is faster with black liquor than with sodium carbonate and that the rate increases with temperature in both cases. Furthermore, carbon dioxide in the reaction gases slows down the reaction rate and no clear influence of pressure was seen on the reaction rate.

The models predicted slower kinetics than the experimental results: this is probably due to the reaction constants in the models, which are extrapolated from experiments at 800-880°C. In this case, the temperatures are between 900°C and 1000°C, which are above the melting point of sodium carbonate (858°C) and closer to the melting point of sodium penta-titanate (1030°C). This might give rise to another mechanism, since the mobility in the material increases when the solids approach the liquid phase.

The reaction rates for the direct causticization reaction between sodium tri-titanate and sodium carbonate were found to be fast enough to be carried out in an entrained-flow reactor system, (e.g. a Chemrec system). Consequently, there is great potential for the combination of the titanate process and the Chemrec process.

NOMENCLATURE

A	preexponential factor in the Arrhenius expression for k (m²/s or m/s)
E	the Arrhenius activation energy (J/mol)
k	reaction rate constant
k_1	the Valensi-Carter rate constant (m²/s)
k_2	the phase boundary rate constant (m/s)
k_3	a constant related to the first order reaction rate (m/s)
k_4	a constant related to the lumped diffusivity (m²/s)
r	the radius
r_0	initial radius of the sphere (m)
R	gas constant (8.3145 J/mol,K)
t	time (s)
T	temperature (K)
x	degree of conversion (-)
z	volume of product formed per volume reactant consumed (m²/m³)

APPENDIX

Since the compressibility factor Z is approximately equal to 1.0 for most of the gas mixtures considered in this case, the gas is assumed to behave as an ideal gas when the gas density and gas volume are calculated. It is very difficult to find literature values for some of the physical and chemical data used in this model, (e.g., the thermal conductivity, k_p, and the emissivity, ε, for sodium tri-titanate or sodium penta-titanate). Consequently, they had to be approximated by values for similar compounds. For compounds such as brick, pyrex, silica, chalk, calcium sulfate, and concrete, the thermal conductivity ranges between 0.35 and 1.4 W/m,K, but salt has a value of 7.1 W/m,K [26]. Furthermore, titanium dioxide has values between 6.5 and 3.3 W/m,K depending on the temperature. Therefore, a value of 3.5 W/m,K for the thermal conductivity was used. In order to study the influence of the thermal conductivity in the model, values between 0.35 and 10 W/m,K were tested; it was found that they all gave almost identical results. A similar approximation was made for the emissivity; compounds such as brick, concrete, silica, porcelain, and glass have an emissivity between 0.6 and 0.93 [26]. Alumina oxide, a highly oxidized metal, has an emissivity of 0.25; values between 0.25 and 0.95 for the emissivity were therefore tested in the model, and it was found that they all gave almost identical results. Consequently, an emissivity of 0.8 was chosen for the model.

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