Wayne Davies B.Sc. (Chem. Eng.) Ph.D. M.I.E.AUST.
Consulting Engineer
Department of Chemical Engineering
University of Sydney, N.S.W. 2006
Telephone: 61 2 692 2256. General Office: 61 2 692 2455. Fax: 61 2 692 2854

Alan Tomlinson
Principal Inversigator
Coalloid Engine Co.

30th October 1992

Dear Alan,

I hope that the following collection of thoughts is helpful. I feel that a list of recommendations is now required and that this list should be composed after consultation with you.

Regards

Wayne Davies

Supercritical Water - A Review, Report and Collection of Thoughts for Coalloid Engine Company

Thoughts on Structure and Solvent Properties

Ordinary water can be thought of as an extended molecular network. The molecules of H2O represent the simplest but not very structural formula for water. As a liquid this material is really a large macromolecule held together by hydrogen bonds i.e. $(H2O)_n$ where n can be a large number (100 or so) which tends to increase as the temperature drops and vice versa. The macromolecules of liquid water is not constant however and the individual H2Os which make them up do not remain with the same macromolecule but exchange with their neighbours at high frequency. This is reason for the use of the term "flickering clusters". The dipole moment of water is high owing to the bond angle of the hydrogen-oxygen-hydrogen configuration which is less than 180 degrees. Electrons attracted to the oxygen make it slightly negative leaving the hydrogens slightly positive. This imbalance of charges gives rise to "hydrogen bonding" i.e. the attraction of adjacent oxygens to hydrogens of a different water molecule. The extended network of these hydrogen bonds gives the unique properties of water that we are aware of, i.e. high boiling point, relatively high viscosity, good solvent properties for polar materials etc. Waters ability to dissolve ionic species is more a function of the dissociation of ions and their hydration by waters than its hydrogen bonding ability.

As the gas, water molecules are effectively in a monomolecular state. The distances between them are too large to allow hydrogen bonding and their kinetic energy is too great to allow molecular interactions to form larger molecules. The dipole moment is still quite high for the same reasons that it is in liquid water, i.e. the bond angle and the electronegativity of the oxygen compared to the hydrogen.

Supercritical water (SCW) can be viewed from two perspectives. It is either (i) the liquid form of water raised in temperature and pressure to the point where liquid water can no longer exist or (ii) the gaseous form of water which has been compressed such that the molecules are forced into close proximity to each other without liquefying. In either case a new state of matter has been produced. The curious thing about SCW is that the dipole moment is very much reduced compared to the liquid form and is comparable to the values of non-polar solvents, eg benzene, aliphatics, ethers etc. which SCW begins to resemble in terms of its solvent properties. This can explained by the following tentative model:

Under the extreme temperatures required for SCW to form, liquid water is not allowed so the extended macromolecular "flickering clusters" are unlikely to exist. Similarly the effectively free monomolecular state of gaseous water is not allowed either. What may happen on a molecular scale is that the waters form ring structures which resemble benzene as shown below (Fig.1).

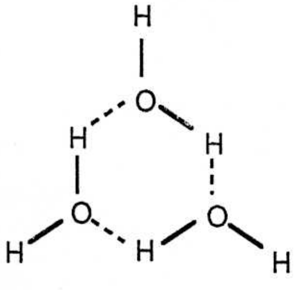

Fig. 1 A Hypothetical Structure for Supercritcal Water

These ring structures form an energetically stable configuration with a high level of symmetry, i.e. the dipole moment is low. The hydrogen bonds are effectively forced into existence because the high pressure which keeps the density of SCW high compared to gaseous water. The molecule now resembles benzene in shape and may even have some aromatic quality owing to the potential for delocalising electrons within the ring. This would explain SCW's powerful **non-polar** solvent properties. Removal of one or more hydrogens from the ring would tend to make this structure even more stable by giving one of the oxygens a negative charge with which to attract adjacent hydrogens more strongly. This electron would not remain with just one oxygen however and it too would be delocalised, stabilising the complete ring structure. This may help to explain the function of alkali eg sodium hydroxide which improves the solvency of SCW for coal. In the presence of alkali one of the hydrogens may be removed from the ring. This would leave a type of hydrated "supercritical hydroxide ion" which then may chelate a sodium ion to give a net neutral complex of relatively low polarity. The fig. below offers a molecular model for this hypothesis.

try to discover some anticorrosive coatings for SS eg Think of anodised alumin for a starter.

see box in ⇐ water gas shift paper Shaw et see colour orig. see Ⓕ

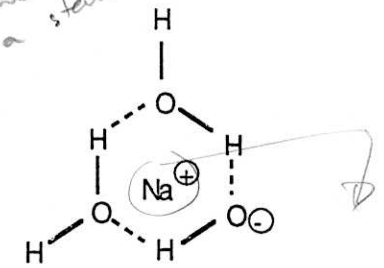

Fig.2 A Hypothetical Supercritical Hydroxide Complex

d-shell

Some conclusions from these hypotheses follow. If sodium forms a complex like the above then potassium would form an even better one. Potassium has a lower energy D-shell of electrons which is more accessible to oxygen's electrons. A complex made with potassium would be more stable than a sodium complex. It may have a lower dipole moment and therefore even better solvent properties for hydrophobic materials.

Why would rapid heating of coal in SCW give better comminution than slow heating ?

The solvency of SCW for coal can be thought of in terms of a non-polar solvent at high temperature attacking a porous coal particle. Firstly consider coal and liquid water together with conditions being slowly raised to supercritical. Under these conditions I imagine the following. Heat applied to the mixture causes the water to become supercritical as the temperature and pressure rise. Water in the bulk outside the coal particles arrives at supercriticality at which time the SCW gradually diffuses into the pores of the coal. Owing to the gentle rate of heating there is very little resistance to flow of SCW into the pores. The gentle rate of diffusion also allows some degree of extraction (leaching) of solubles within the coal pores which are carried **into** the pores with the fluid. This process concentrates the solubles in the "core" of the coal particle leaving enlarged pores in the wake of the SCW. When the pressure explosively reduced through the heavy duty pressure reduction valve, the coal particles explode by virtue of the rapidly expanding SCW.

Under rapid heating of coal and liquid water together a different model emerges: Each coal particle is a heat sink. Heating the bulk of the coal-water slurry causes causes heat to firstly enter the water. Heat from the water is then transferred to the coal particles. Because they are relatively cooler, each particle of coal will be surrounded by a layer of liquid water even while the water in the bulk is going supercritical. The large and rapid increase in pressure in the bulk will initially force non-critical water into the pores of the coal particles. Very soon after this the temperature and pressure will be everywhere the same and the water inside the pores will be supercritical also. The effect of this is that the non-critical water on its way through the pores will be a **poor** solvent for the largely hydrophobic solubles in the coal. There will be less leaching and less concentrating of solubles in the core of the coal particle. This will leave the pores smaller than in the slow heating case above. Upon explosive release of pressure the smaller pores will act as a greater resistance to flow and cause the SCW inside to apply a high internal pressure to the coal particles which explode them more efficiently. In the former case the pores will be relatively enlarged so they offer less resistance to flow and the SCW flows out from the pores more easily offering less efficient explosive comminution.

Recovery of Waste Heat for Supercritical Extraction

Gas temperature from a gas turbine exhaust may the correct temperature for SCW but the heat transfer with feed flowing inside a tubular reactor will probably be limited by the gas film resistance on the outside of the tube. The solution is to calculate the heat transfer coefficients for hot gas (outside) and water-coal slurry (inside) and determine if it is possible for the narrow tubing that you use as a reactor. Fins may be needed on reactor tubing and the whole thing to be inserted into the hot gas stream.

Separator Design

The reaction of SCW with coal fines makes char, "coal tar extract", gas and mineral ash as products. Char may be the most valuable of these. I see a reactor scheme for a continuous process using cyclones to separate the fractions before letting down the pressure to that of inlet to an engine or other combustor. Cyclones would probably be designed as gas cyclones for supercritical water (because SCW fills the vessel completely like a gas) but would operate more like hydrocyclones bcause the fluid density is more like a low-density liquid. Separation should be easy as the density of SCW is low compared to the solids (ash at 2.5 and char at 1.2). A battery of cyclones could be placed in series so that the most dense material discharges first i.e. mineral ash. In the next cyclone the solid to be discharged would be char. A detailed design is possible using the standard hydro and gas cyclone equations.

At this point the temperature of the reamining stream of SCFF could be let down, using a heat exchanger, to below supercritical, causing the water to separate out as a liquid. The change in polarity would cause the "coal tar extract" to separate out as an oily dispersion in the water phase. Gas derived from the effective pyrolysis of the coal by SCW would form as a separate phase above the water. This could be taken off easily and used in combustion for instance. The oily dispersion of coal tars in water could be used as a fuel directly or could be concentrated (by using gravity settling in a high rate plate thickener for instance) such that some of the water could be recycled leaving an enriched tar for combustion.

Both mineral ash and char would be removed from the process via the "oversize cuts" of their respective cyclones. These streams would contain ash and char in a concentrated form in the SCW-extract of the whole coal. A special design for the removal of solids from the high-pressure conditions would be required. This may rely on a series of step-down valves such that the slurry of solids can be let down gradually and exhausted to atmospheric pressure. Another perhaps more elegant way would be via an energy recovery machine such as a small reciprocating engine connected to a load or by so-called flutter valves (valves whose net rate of flow is governed by their rate of opening and closing fully). These solid streams could be taken off in such a way that the SCW and other volatiles flash off leaving a clean and dry solid behind. The vapours resulting could be combined with the mainstream of the SCFF and put to combsution. This separation problem resembles mineral extraction and processing in which the extracting fluid is high pressure (SC) water instead of liquid water. After extraction the problem is to separate the solids from the extract. This is usually done by using thickeners, hydrocyclones, centrifuges, filters or evaporaters. The same unit operation approach will be useful here.

At first glance I feel that it is easier to cool the SCW-extract to sub critical rather than to drop the pressure (while keeping the temperature high). In the former case the volume of material is kept low. Subsequent separation steps using physical methods, can be carried out in relatively small-scale equipment, albeit designed for high-pressure operation. In the second case the reduction in pressure will cause a large increase in gas volume which will require correspondingly larger separation equipment. This is offset somewhat by the lack of requirements for high-pressure design. It may be that a clever design will use both a drop in temperature for a particlar separation step and this could be followed by a drop in pressure to facilitate another separation step.

Use of Solvents other than Water in SC Extraction.

Without examining these in particular I feel that any solvent other than water which has been used for SC extration will add a significant cost to the process which will make it uneconomic. The recovery of solvent for recycle will be significantly less than ideal (100%) so the incremental cost of the added solvent will be high. Literature on other solvents is useful because it will add to the understanding of the processes and will help in defining a model (qualitative or otherwise) for the processes.

Fate of Sodium Hydroxide used to Augment Process

It is a chemical engineering truism that input equals output plus rate of accumulation. If NaOH were added to the coal-water slurry to prevent agglomeration and to assist in extraction, then this NaOH would probably report to the final aqueous stream emerging from the process. If this stream were put to a heat engine then the caustic may cause problems with its mechanical operation. In this case it would be desirable to separate the liquid coal tar material from the aqueous stream such that the latter could be recycled. This could be achieved by allowing the SC water to cool to sub critical temperatures at which point the now liquid high pressure water would separate out from the oily coal tar.

It is likely that phenols present in the pyrolysate of coal (made by SCW hydrolysis of amines) would be in the water phase however because phenols act as weak acids forming phenolate ions. A similar argument can be made for hydrogen sulfide. Thus recycle of the alkaline water would also recycle phenols. These would accumulate in the water recycle loop and without a means of removing them eventually the process would cease to run. Without recycle of NaOH/water the plant would give rise to an aqueous waste water stream containing environmentally difficult materials probably requiring expensive processsing before discharge to sewer. Separating the phenols from the SCW extract before it is droppped to sub critical would be difficult also. Phenols have been extracted by SCW so it is reasonable that these will not spontaneously fall out of "solution" in SCW. Addition of acid may help here but this would mean neutralising the expensive NaOH which has been added.

Thoughts on the Provisional Patent Application (Hoare and Tomlinson)

The reactor for the production of supercritical fluid fuel (SFF) should be a tubular (plug flow) reactor. This has many advantages.

- A tubular reactor gives the greatest degree of conversion and the most uniform product for most reaction types (e.g. first or higher order reactions where the greater the concentration of reactants, the greater the reaction rate).
- Tubing can be made to contain pressure at lower costs than tanks or vessels. Tubing or pipe is not designated officially as a pressure vessel until it is above 5 inches diameter. This obviates the need to get certification.

- Heat transfer to a tubular reactor is made easier than a tank because of the large surface area. This area can be augmented with fins if necessary.
- Reactor volume can be made to any desired size by selecting the diameter and length of the tubing.
- Especially useful in the development stage of a process is the ability to monitor reaction progress. This can be done by removing samples from any point along the reactor length via T pieces and valves. This leads to more efficient and faster process development times.

A process based on a tubular reactor will result an emerging stream of SC water together with products of the reaction with coal. This will require subsequent separation steps to remove the other products as reviewed above.

Presence of Sulfur, Vanadium and Nickel in SCFF – not in coal as much as sump oils

Ni V S
not many waste
oil not coal

Nickel and vanadium are present in petroleum in the form of porphyrins and these are probably present in coal also suggesting its plant origin as chlorophyll. They are removed incidentally when fuel oil is treated by hyrodesulfurisation. I think this is process which removes sulfur by exploiting a redox reaction between sulfides and sulfur oxides such as SO_2. It is convenient because it precipitates elemental sulfur, i.e.

$SO_2 + 2 H_2S \rightarrow 2 S + 2 H_2O$.

S in Aust coal 0.5-1 %
S in waste oil 3 %
500 ppm
V " " 80 ppm
Ni " "

The same treatment may reduce V and Ni from their ionic to their metallic forms. If so then these would probably emerge with the elemental sulfur. I would see sulfur removal as a problem which might be tackled by using oil refinery technology. Its not cheap I understand. Another way is absorption over lime. This would require a solid/gas contactor such that the lime as $Ca(OH)_2$ absorbs and "sweetens" the fuel product. As levels of sulfur increase the cost of this operation naturally goes up too. The product might be a mixture of calcium sulfites and calcium sulfides which would require disposal also, perhaps by a biotreater.

Under SCW extraction V and Ni might be removed in any chemical form at all possibly as complete porphyrins. More understanding of the chemistry needed here. If however alkaline SCW were used (i.e. SCW with 0.5 M NaOH) then it is more likely that the sodium would replace these metals and give a free organic molecule which might end up as char and free nickel and vanadium as cations. These might be removed by ion exchange as discussed below. The problem is however that once 0.5 M NaOH is in the system it is more difficult to remove the contamionating metals by ion exchange. The high concentration of negative hydroxide ions tends to compete with the negative charges on the resin for available (positively charged) cations like Ni and V. It might be best to allow the metals to remain in the char and let someone else deal with it as required.

Separation of Salts from Fuel

fix this

Presence of salts in SCF fuel may be problem especially if its ultimate fate is a heat engine. Distillation is the oil refinery method of removing non-volatiles. Some "salts" are volatile of course because they are not really salt but organometallic compounds. There may be a case for

Na is a problem - slagging on turbine blade
SECV paranoid about Na. < 0.2 ppm.

These are balanced – coal in elect out.

No say Alan

using the residual waste heat from heat engines, especially turbines, for distillation of the tar oils. The plant would begin to resemble a small refinery however and the engine would start to look like an afterthought. This is unattractive at first glance.

A reasonable alternative may be to pass the oil-in-water dispersion of coal tars into an ion exchange column. If the SCFF is in water already then we can exploit the preferential solubility of salts in the aqueous phase. Treatment in an ion exchanger would remove the cations and the anions and replace these with hydrogen and hydroxide ions respectively. These neutralise each other and we are left with neutral water which is present anyway. The likely problem here would be mass transfer of salts from the oily phase. Given that salt is not highly soluble in SCW the salts are likely to be present in the oily phase while ever the whole extract is supercritical. When the temperature or pressure are dropped below that requires for supercritical conditions, the salts will be less soluble in the oily phase and will be happier in the water phase. Mass transfer from oil to (liquid) water is likely to be the rate-limiting parameter. Good mixing and small particle or droplet size are important. High temperatures usually imply fast mass transfer rates because of low viscosity and high molecular velocities indicating that both the bulk and microscopic parameters are favourable. One problem might be to keep an ion exchanger intact at scalding temperatures. We could use molecular sieves for this instead of plastic resins used in laboratory water deionisers.

Conclusions

We could design the reactor and separator train as follows: A tubular reactor possibly fitted with fins could be used for the formation *in situ* of SCW. This would extract the coal fines and form the "crude" SCFF. As above it would be feasible to remove mineral ash and char via cyclones. This would be followed by a drop of T or P to below critical at which point the coal tar/oily material would drop out as a dispersion in liquid water. This dispersion would then be passed over an ion exchanger and salts removed from the water phase. If removal of Ni and V were required then the next stage might involve addition of caustic soda. Sufur could be removed by hydrodesulfurisation or possibly by absorption over lime. Although distillation might at first glance seem unwieldy for the overall process, the abunndant waste heat present may make it a possibility. The whole design is very much dependent on the nature of the economically attractive product, i.e. is it char or fuel for engines or something else.

Answer 2 Things - both an engine and a fuel plant
plant makes sense with free heat.
Aust. needs to export more. Can't sell more coal
∴ turn it into Al for instance. ⇒ 2nd industry
power stations.
coal — gas turbine → min capital cost
either molten salt or supercrit water → research money
in these area. → gasifier at 1000°C
or lower temps at