

**Kettle Saponification - Computer Modeling -
Latest Trends and Innovations**
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This text is not designed to be a self-contained primer on the production of kettle soap via the full boil kettle process. It is designed to demonstrate an original method of doing same, utilizing the computer to achieve a high degree of accuracy in process control.

HISTORICAL INFORMATION

Most readers will recall my prior work on this topic (1). At that point in time I was under contract with Bradford Soap, and a condition of my publishing the prior work was that I had to make it difficult to understand. I am under no such obligation now, so every effort will be made to make this complex topic comprehensible. I apologize for the constraint of my earlier work.

DEFINITIONS AND TERMINOLOGY

The terminology is the same as my prior work, and is included here for completeness.

The symbols in the curly brackets { } will represent the shorthand notation used in the algebra.

Processing Steps - will be represented by sequential numbers spanning 0 to k+1, with 0 being the loading and k being the number of washes. The processing step will be represented as subscripts when applicable.

Ingredients - the materials which are either added to or removed from the kettle. The ingredients will be represented as subscripts when applicable. They includes:

$\{f_1, f_2, \dots, f_i\}$ Fats and oils (total number = i)

$\{a_{i+1}, a_{i+2}, \dots, a_{i+j}\}$ Fatty acids (total number = j)

$\{c\}$ Caustic - 50% solution of NaOH and H₂O

$\{b\}$ Brine - saturated solution of NaCl in H₂O

$\{l_0, l_1, l_2, \dots, l_k\}$ Lyes generated by process steps ($k = \#$ of washes, $k = 0$ is the spent lye for glycerol recovery) - solutions of glycerol, NaCl, NaOH and H₂O

Spent Lye - a byproduct of the kettle process which is high ($>15\%$) in glycerol, and low ($<0.5\%$) in NaOH.

Wash Lye - a lye which is generated and consumed by the kettle process

$\{y_0, y_1, y_2, \dots, y_{k-1}\}$ Lyes added to process steps

$\{u_0, u_1, u_2, \dots, u_k\}$ Curd ($k = \#$ of washes, $k = 0$ is the curd resulting from loading) - an intermediate remaining after lye removal

$\{n\}$ Neat - the finished product of the kettle soap process

{r} Seat [or Nigre] - remains in the kettle after neat soap removal.

{w} Water - the liquid phase of H₂O

{t} Steam - the vapor phase of H₂O

Components- the chemical compounds present in the ingredients.

The components will be represented as superscripts when applicable.

They include:

{s} Soap

{ω} H₂O

{g} Glycerol

{d} Sodium chloride [NaCl]

{h} Sodium hydroxide [NaOH]

Physical properties - quantitative characteristics of the components and/or ingredients. They include:

{M} Mass (lbs)

{X^χ} Mass fraction of component χ (lbs/lbs)

{W} Molecular weight (lbs/lb-moles)

{T } Temperature (°F)

{ ρ } Density (g/cc)

{ P } Heat capacity (BTU/lb°F)

{ Γ } Heat of reaction (BTU/lb)

Miscellaneous Parameters

{ \bar{T} } Reaction Temperature of kettle (220°F)

{ D } Day of the year

{ $E_0, E_1, E_2, \dots, E_{k+1}$ } Electrolyte settling ratio (where $k+1$ is the finish step)- the ratio of the different electrolytes as they settle through different phases, specifically, $\frac{[NaCl]}{[NaOH]}$

{ δ } Separation efficiency - the fraction of the available lye which separates from the curd phase.

{ G } Glycerol concentration factor - this is a measure of glycerol's preference to concentrate in the lye phase during phase separation.

Cooling constants determine how fast the kettle cools. These values are site specific and are a function of the kettle geometry, insulation and environment. They include:

{ T_∞ } Equilibrium temperature (°F)

$\{D_T\}$ (Half life Days)

Evaporation constants determine how fast the kettle loses water due to evaporation. These values are site specific and are a function of the kettle geometry, insulation and environment. They include:

$\{Q_\infty\}$ H₂O loss at infinite time (°F)

$\{D_\omega\}$ Half life (Days)

Conservation equations - Since matter and energy can not be created nor destroyed, we can use that principle in our analysis of the kettle process. We apply this in three distinct ways. They include:

Conservation of mass

Conservation of mass of each component

Conservation of energy

Kinetics -

The saponification reaction is not spontaneous. As described in Woollatt p. 154, "... the reaction with neutral fats ... does not start readily. It is autocatalytic, that is catalyzed by the product of the reaction, soap. Hence, the reaction rate accelerates greatly until most of the fat is reacted, when it slows down again." The secret to successful computer simulation is to keep things as simple as possible, but not too simple. The reaction time is much less than the

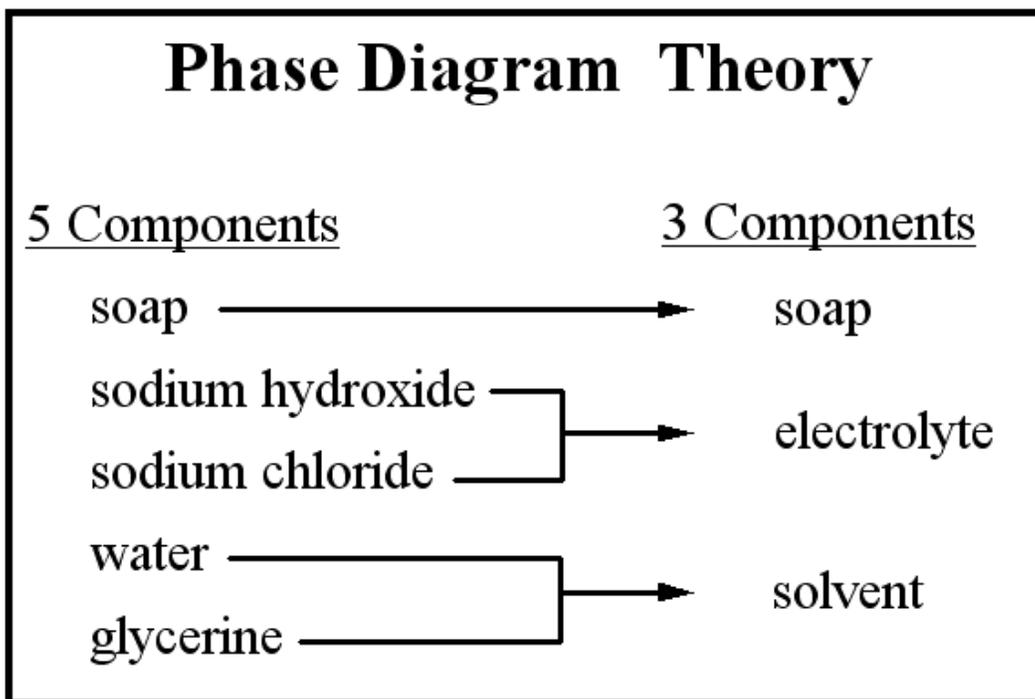
batch time. One simplifying assumption we can make is that everything happens instantly.

PHASE DIAGRAM THEORY

This section is also identical to my previous work and is included here for completeness.

The kettle soap process has 5 components and strictly speaking, a 5 component phase diagram is required to represent it. This is too complicated. We simplify the diagram into a three component system. The components are soap, total electrolyte, which is a linear combination of the sodium chloride and the sodium hydroxide present and solvent, which is a linear combination of glycerol and water. See Figure 1.

Phase Diagram Theory



[Figure 1 here]

The Component list is then simplified to include:

{s} Soap

{v} Solvent

{e} Electrolyte

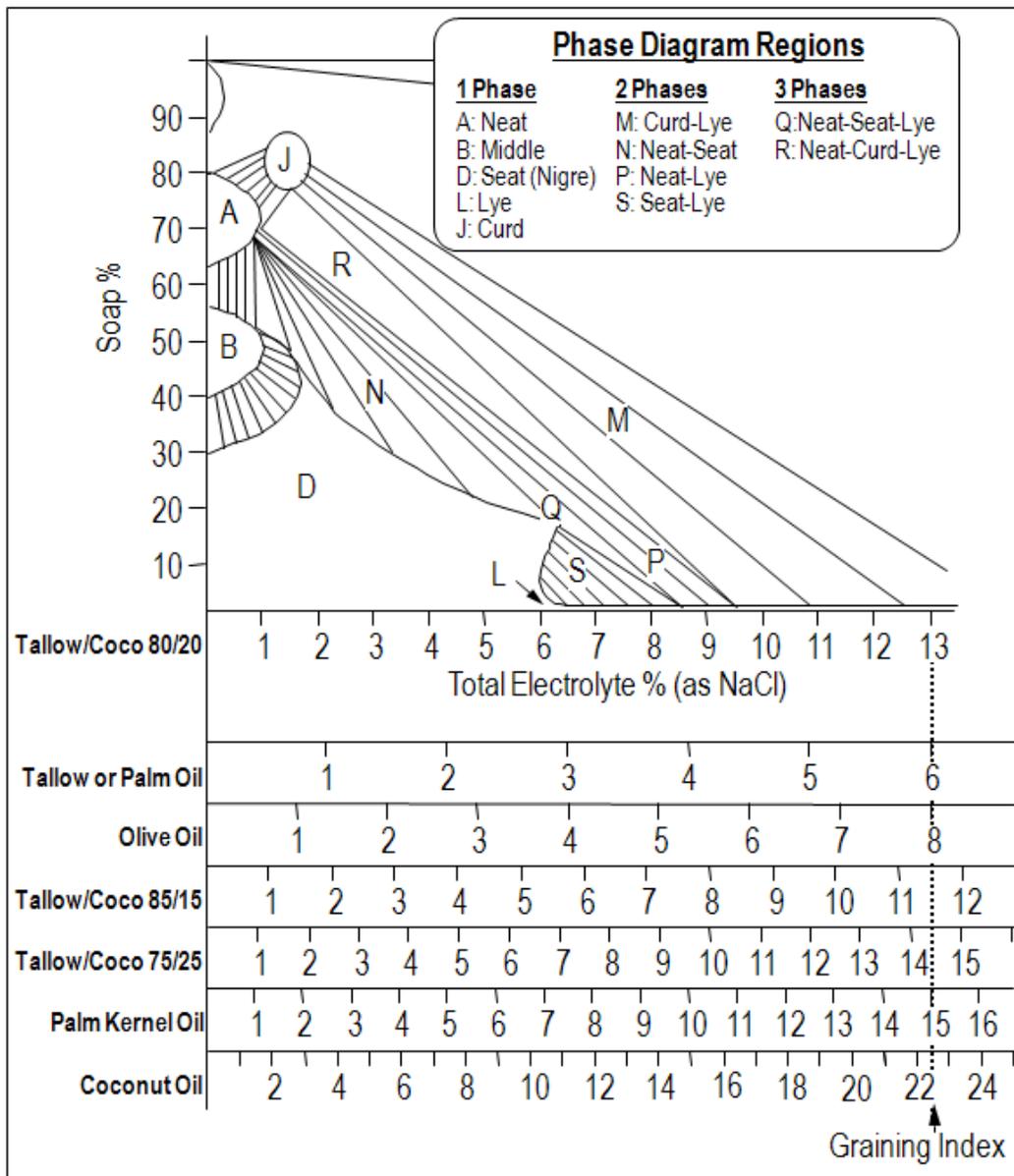
with the linear combinations defined as:

$$M^e = z^d \cdot M^d + z^h \cdot M^h \tag{1}$$

$$M^v = M^w + M^g - (1 - z^d) \cdot M^d - (1 - z^h) \cdot M^h \tag{2}$$

Here, $\{z\}$ is defined to be the "graining efficiency", a traditional soapmaking term, is a measure of how much of the particular electrolyte will have to be added to move the resultant mixture a certain distance in the x direction on the phase diagram. Other electrolytes can also be used as described in Spitz (2), p.119. Typically, the "z" factors are normalized such that $z^d = 1$. Equation (1) determines the total amount of electrolyte present. Equation (2) determines the total amount of solvent present. The final two terms in equation (2) are necessary to assure that the conservation of mass components are maintained.

The phase diagram of a typical 80/20 tallow/coco soap as illustrated in Woollatt (3) p. 153 is illustrated in Figure 2.



[Figure 2]

Also note the inclusion of several “X” axis. The values for the “X” (electrolyte) axis depend upon the chain length distribution of the soap. The graining index data presented in Spitz (2) p.118 allows us

to determine the phase diagrams for a number of different soaps. The relative graining indices are aligned and the electrolyte is scaled in proportion to yield the phase diagrams for all listed soaps. As a first order approximation, the “X” axis is scaled in proportion to the graining index. For example, the coordinates of the point of intersection of the “D” and “Q” regions occur at 6.3% electrolyte for the 80% Tallow/10% Coco soap illustrated in Figure 2. This soap has a graining index of 13. A pure coconut oil soap with a graining index of 22.5 will have the point of intersection of the “D” and “Q” regions at $\frac{22.5}{13} \cdot 6.3\% = 10.9\%$. In this fashion, phase diagrams for soaps of all chain length distributions can be determined.

The phase diagram is further approximated for computerization. Only the two phase regions M and N are required for modeling. Both regions are approximated by straight edged quadrilaterals, i.e. linear approximations, which have proven to be sufficient. Higher order approximations (quadratic) have been tested. The higher order approximations complicate the mathematics but do not provide any improvement to the model. A specific linearized phase diagram will be discussed below.

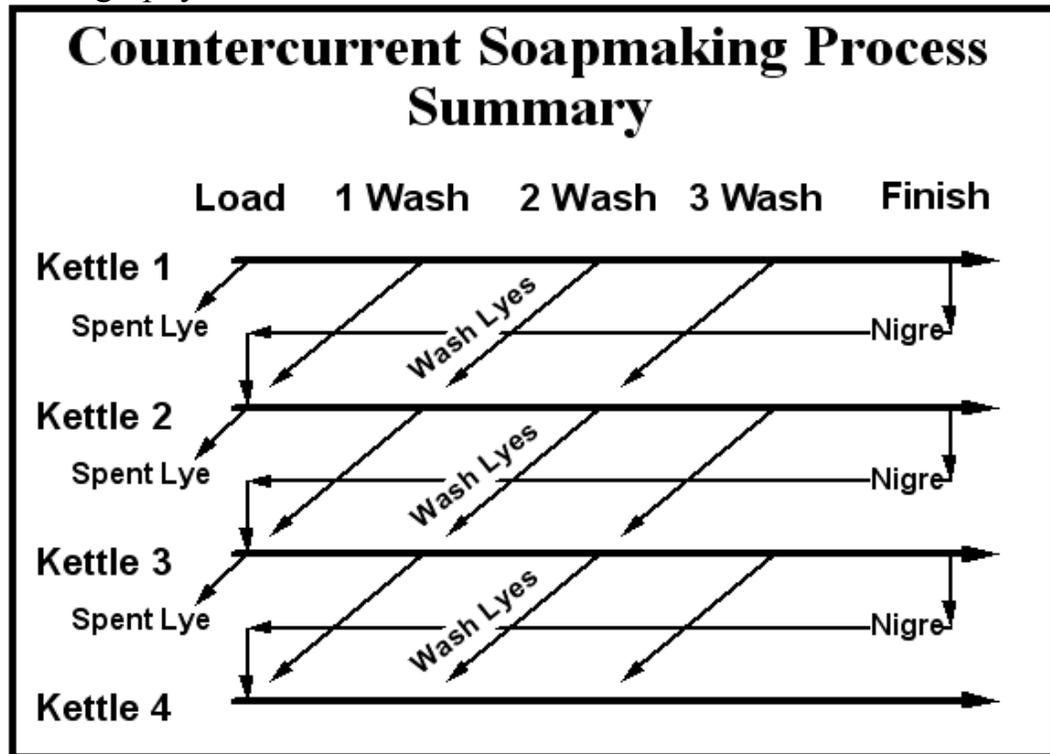
KETTLE SOAP BOILING - GENERAL DISCUSSION

Since the publication of my prior work, the rising cost of energy and raw materials and the plunging value of glycerin have resulted in a

paradigm shift in the types of kettle processes employed. We consider the following processes:

1. Counter Current or Full Boil: The traditional way of processing a kettle of soap. In this process, one generates a low glycerin (<3%) neat soap, a seat and spent lye with 15% or more glycerin. The steps involved with generating lyes are relatively forgiving, settle quickly and are easy to manage. The finishing step requires a 'Fitting' of the kettle. The Fitting brings the kettle to a state where the neat soap separates from the seat over a 24-96 hour period. This Fitting is difficult to achieve and leaves open the possibility that an acceptable neat soap will not be available after the prescribed settling period, resulting in process interruption and considerable rework. Even if neat soap is successfully produced, the quantity of neat soap may vary significantly from batch to batch because of the difficulty in reaching the best Fit. This process is fully outlined in many sources sited in the

bibliography.



2. Semi-boiled: I prefer to call this process “Seatless”. In the Seatless process, an empty kettle is loaded, saponified and finished in one step, leaving all of the glycerin (~8%), color and odor in the neat soap. Neither Seat nor Lye is generated, and the soap is ready for drying in as little as 4 hours after the loading commences. This high level of glycerin provides considerable ‘Nomar’ qualities, but sometimes results in a base that will ‘sweat’ and stink under high humidity conditions, and will display more cracking than a full boiled kettle.

3. Lyeless: This process loads an empty kettle to allow the kettle to be finished directly. The resulting neat soap is available in 24 hours at around 5% glycerin content, leaving behind a seat containing many of the color and odor bodies. This process is advantageous if one has an outlet for the seat in a lower grade base. The physical properties of this base will be intermediate to the bases outlined in 1 and 2 above.
4. Oil Finish: This process loads either an empty kettle or a seat, and generates one or more lyes in the same fashion as the full boil process. Unlike the Full Boil process which has the finicky and time consuming Fitting, the resulting curd of the Oil Finish process has a very low Sodium Chloride content, allowing for the addition of a high quality fat (e.g. Edible Tallow), oil (e.g. Edible Coconut Oil), fatty acid (e.g. Coconut Fatty Acid) and/or Citric Acid to consume the excess free alkalinity and result in a kettle containing only a low glycerin (<3%) neat soap.

Step 1 - Loading

Typically, a kettle of 20,000 to 200,000 pound capacity is used. The seat often remains in the kettle from the prior batch. The seat is brought to a boil by the introduction of live steam into the bottom of

the kettle, through a specialized nozzle called a rosebud (because of its appearance), and through a series of open steam coils.

Precise amounts of fats, oils, and/or fatty acids are combined with caustic, brine, and water. In the case of the counter-current process, recycled lyes from the first wash of a prior kettle are also added. The materials are added such that the rate of saponification is maximized.

Since "Spent" lye is the desired output of this kettle, the electrolyte or "X" axis of the phase diagram should be composed of only NaCl, with only enough NaOH added to the kettle to saponify the fats, oils and fatty acids. This poses a problem for the soapmaker, since high excess levels of NaOH drive the saponification reaction to completion, however, there should be no excess, and perhaps even a slight deficit of NaOH, at the conclusion of the loading process to assure formation of a "Spent" lye.

The Seatless process magnifies this problem. Since in this process the kettle is loaded and directly pumped, the Soapmaker must assure that all of the fat and oil has been completely saponified and the free NaOH must be very low. Attempts at loading a seatless kettle without sophisticated mass flow meters to precisely measure the fat, oil and caustic additions have not been successful. However, with precise calculations and measurements, an experienced and motivated Soapmaker can be very successful in loading and finishing a Seatless

kettle in a timely fashion. Although I have had great success using only whole fats and oils in the seatless process, the problem of achieving a fully saponified kettle with a low free NaOH (<0.05%) is simplified if one has some fatty acid or Citric acid available to neutralize the last bit of free NaOH after all of the fats and oils have been saponified.

We now turn our attention to identifying the region of maximum saponification on the phase diagram. It is slightly lower in electrolyte than Region M (the two phase curd-lye region). The exact region this area is located in is subject to some debate. Most published phase diagrams illustrate three distinct regions, those being M, P and R, however, it is our experience that for all practical matters those regions are indistinguishable during the production process. That being the case, the point of maximum saponification will occur in Region Q or perhaps even Region N.

The actual "location" of this point of maximum saponification with regard to Region R, P, Q, N, etc. is inconsequential, when one's principle priority is optimizing production. An experienced soapmaker inherently knows this region by the appearance of the kettle contents. To identify this crucial point in the soapmaking process, simply sample the kettle at the point when the experienced soapmaker "knows" the kettle "looks" best. 10 to 12 kettles should be more than enough data to define this point for the fat and oil blend

being used. Once the first fat and oil blend has been identified, other similar blends can be extrapolated using the relative graining index method outlined above.

The strategy outlined in the preceding paragraph deserves additional attention. Traditionally, there have been two separate and distinct approaches to optimizing the kettle process (as well as all processes). Since the dawn of time, manufacturers have relied upon trial and error to optimize any process (observation). More recently, application of the laws of physics and technology has been applied to fully understand and optimize the process. Both approaches can be time consuming. I have always advocated and implemented a hybrid approach, breaking the large problem down to a series of smaller ones, and deciding step-by-step if the answer can be more quickly ascertained through observation or application.

The percent soap, or "Y" axis has a limited working range, since levels in excess of 55% soap result in a mixture which is too viscous to permit good agitation using only live steam, and levels below 40% result in excessive amounts of spent lye, reduced kettle capacity, and low glycerol concentrations in the spent lye.

Remember that the loading starts not with an empty kettle but with a nigre, which should have a composition on the border between Region D (the one phase nigre region) and Region N (the two phase

neat-nigre region). The loading should proceed to bring the partial contents of the kettle to the saponification point ASAP, and then keep the kettle composition at the saponification point for the remainder of the loading process.

Step 2 - Graining

After all of the fats, oils and/or fatty acids have been saponified, the kettle needs to be positioned on the phase diagram at a point which will result in an unstable mixture of Curd and Lye. This area is in Region M (the two phase curd-lye region). Only a limited area in Region M will effect good separation of the lye from the curd, this area being just over the border from Region R. Complicated interactive forces at the molecular level exceed gravitational forces, thus the lye and curd do not completely separate. The percentage of total separation is the "separation efficiency", in which 83% seems to be a realistic maximum for industrial kettle soap processes.

Movement away from this border results in an "over-graining" condition where even though the lye and the curd are two distinct phases, quite visible to the naked eye, they do not separate. In these cases, separation efficiencies can drop below 50%, yielding a process which cannot be economically viable, since the resulting curd will not be high enough in soap percentage to allow for effective fitting.

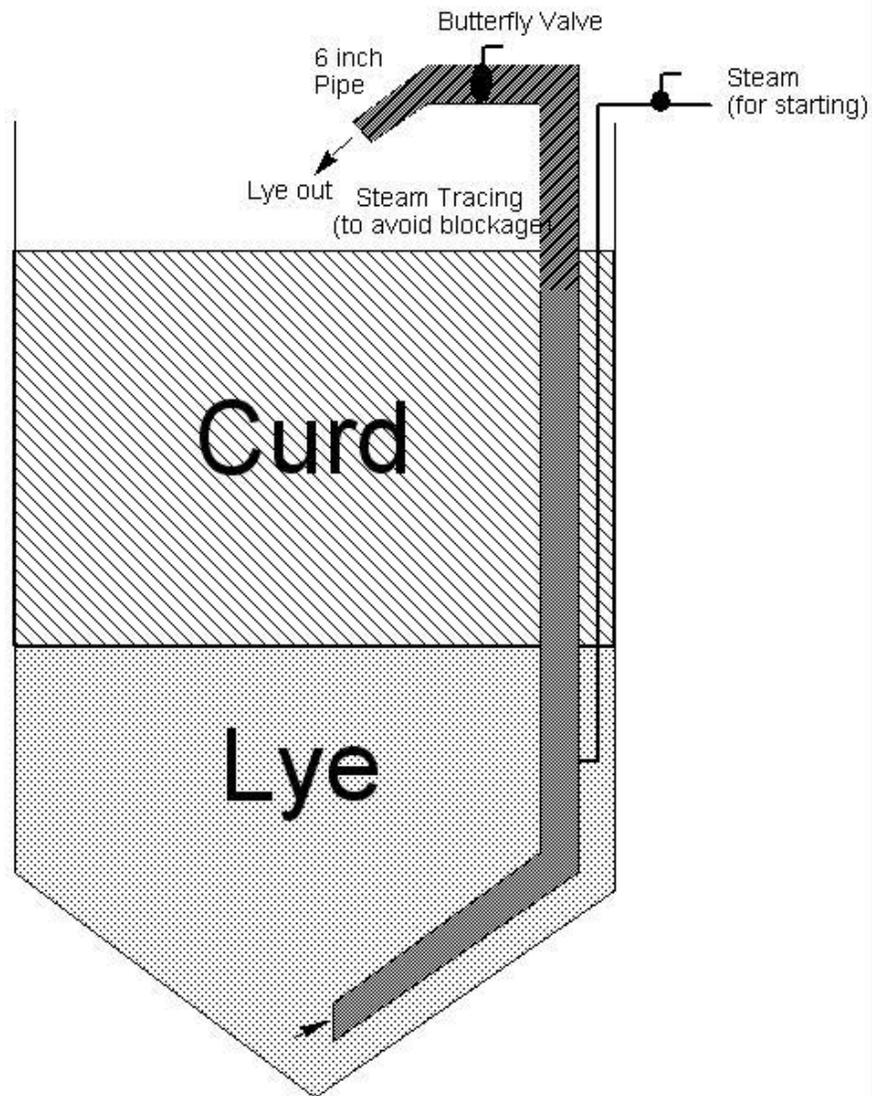
Movement from Region R to Region M is done by the addition of brine. In theory, this could also be done by the addition of rock salt, if the amount of generated lye needs to be minimized, or by the addition of NaOH if the presence of excess NaOH in the (now not) spent lye is acceptable. This process is called "graining" the kettle since the kettle's appearance changes from being smooth to being very grainy. There are a number of traditional Soapmaker checks which can be made to assure that the proper grain has been achieved. These tests are discussed in the traditional references outline by Tom Woods (1).

Note - Again, the exact point of "best" settling is known by the experienced Soapmaker. Sampling a small number of kettles will define this point and allow the computer to bring the Soapmaker to this point on a routine basis.

The efficiency of kettle agitation can be enhanced by installation of a "Recirculation Pipe" as depicted in Figure 3.

Kettle Recirculation Pipe

- improves mixing during loading and washing
- allows soapmaker to sample lye



[Figure 3]

This recirculation pipe allows lye which accumulates on the bottom of the kettle to flow up the pipe and be disbursed on the top of the kettle. This process allows for more rapid saponification and full consumption of the NaOH. The recirculated lye can be sampled and tested for both free alkali and salt levels. Once the desired levels are achieved, then the graining process is considered complete. The desired levels are determined from the phase diagram by constructing a "tie line" which passes through the graining point. The intersection of this tie line with Region L (the one phase lye region) determines the electrolyte concentration. The absence of free alkali in the recirculated lye sample indicates that the saponification reaction is complete.

Step 3 - Settling and Spent Lye removal

The kettle is allowed to settle, which results in an accumulation of lye at the bottom of the kettle. The composition of this lye is predicted by the use of the tie line as described above. The total quantity of lye is determined by the ratio calculation standard to all phase diagrams. The available lye is determined by multiplying the available lye by the separation efficiency, remembering that 10% or more of the available lye cannot be removed without the aid of increased gravitational forces (e.g. a centrifuge).

A properly grained kettle can have lye removal occur almost immediately. This immediate removal of lye does not come without a price, however. The solubility of soap in the lye is a partial function of the lye temperature. Lye removed immediately upon graining will have temperatures in excess of 220°F, and will carry with it in excess of 1% soap. Upon storage and subsequent cooling, this soap will precipitate out of the lye and float to the surface, eventually creating a solid mass inside the lye storage tanks. This soap can be added back to subsequent kettles but requires management to assure lye storage capacity is not clogged with precipitated soap. Kettles allowed to settle for longer time periods will yield cooler lyes and less precipitated soap problems.

Counter-current processing will net glycerol concentration in the lye in excess of 15%. Concurrent processing (i.e. lack of counter-current processing) will yield spent lyes with less than 12% glycerol.

The exact concentration of glycerol in the lye can be calculated once one considers the mechanisms at work. The solvent in the simplified phase diagram consists of glycerol and water. Upon completion of the graining process, there is a definite ratio of glycerol to water in the solvent. One of three mechanisms can occur: the ratio of glycerol to water can increase in the solvent rich or lye phase relative to the entire mass of the kettle, the ratio can stay the same, or the ratio can decrease. The first mathematical models of the system assumed that

the ratio was constant throughout. Comparing actual results to the model netted slightly higher glycerol concentrations in the lye than predicted. A glycerol concentration (or "fudge") factor was defined. A value of 1.1 matched the model to the actual results, meaning that glycerol had a slightly higher tendency to migrate into the solvent rich or lye phase in preference to the water.

Step 4 - Kettle Washing

Washing is the process of adding additional amounts of caustic, brine and water to a settled curd. Remember that the settle curd is located in Region M, close to Region J (the single phase curd region).

Washing moves the kettle composition down the tie line towards Region L. Again the same constraints apply with regard to overgraining the kettle.

The washing is performed for several reasons. First, the color and odor of the soap is improved. Second, the concentration of glycerol in the soap is reduced. Third, the free alkali to salt ratio is controlled. The loading and graining steps require the generation of a "Spent" lye, in which the electrolyte is composed purely of NaCl. Since the spent lye is removed from the kettle process and used as the feedstock for a glycerol evaporator, it is important to minimize the free alkali content to reduce the treatment costs associated with glycerol recovery. Thus the free alkali to salt ratio is effectively "zero". Such

high levels of salt, if carried through to the neat soap, will produce a rice so high in salt that subsequent processing and bar pressing will be severely compromised, if not impossible. By washing the kettle with precise amounts of caustic and brine, the free alkali to salt ratio can be shifted to provide a soap base with superior handling characteristics.

This is carried to the limit with the Oil Finish process. Here, the NaCl level of the settled curd has to match the finished Neat soap specification. Applying Caustic washing, without any additional Brine added during the washing step(s), rapidly lowers the NaCl levels to allow for Oil Finishing. Please refer to the next section for more on this topic.

The washing is performed in such a way as to bring the kettle to a point of instability (as described in the graining step above). Again, the recirculation pipe is utilized to effect better mixing and to allow sampling of the lye. Once the recirculated wash lye has achieved the desired free alkali and salt concentration, the washing is complete.

Step 4A – Washing an Oil Finish (OF) Kettle

The principle for washing an OF kettle is identical to described above. However, the goal of the OF wash is to leave 0.5% NaCl in the curd. Since the total electrolyte level is dictated by the physical chemistry of the phase diagram, one has to grain the kettle out with

just Caustic instead of the traditional Brine and Caustic mix. This “Caustic Wash” has another unique property; the resultant unsettled Curd has a very unique appearance. The unsettled Curd has a very small grain that looks like wet sand. If properly balanced, the lye drops out very quickly, allowing one to proceed directly to the Oil Finish step and completion of the kettle. The challenge here is to effect a complete separation, so that the settled Curd is low enough in moisture (<32%) so that when the kettle is finished, the soap is indeed all Neat soap and not a mixture of Neat and Middle soap. This problem can be somewhat mitigated with the use of Citric Acid during the Finishing.

Step 5 - Settling and Wash Lye removal

The kettle is allowed to settle, which results in an accumulation of lye at the bottom of the kettle. Again, lye removal can proceed almost immediately if the kettle has been properly grained. This lye is stored and is used during the loading of subsequent kettles. A properly designed kettle process will yield an amount of lye from a wash to match the amount of lye to be recycled back into the prior step of the subsequent kettle. The computer model can greatly simplify this problem as will be demonstrated later.

At the conclusion of lye removal the kettle is in Region M, with the best location being as close to Region J as possible, meaning most of the lye being removed.

Steps 4 and 5 can be repeated as many times as necessary to achieve the proper color, odor, glycerol concentration and free alkali to salt ratio. Diminishing marginal returns occur after two well-defined washes.

Step 6 - Finishing or Fitting the Kettle

It is this step which traditional soapmakers appear to hold as most mysterious and skillful. However, a properly designed kettle soap process will result in very consistent finishes. At the start of this step, the kettle has been drained of all available wash lye and the desired free alkali to salt ratio has been achieved. The kettle is in Region M close to Region J. Water is used to finish the kettle. Addition of water to the kettle moves the kettle's composition directly towards the origin on the phase diagram. The kettle passes through Region R (the three phase curd-seat-lye region), and into Region P (the two phase neat-lye region). It would be nice if effective settling would be possible in Region P, since this would yield only neat soap and lye, however, this is not observed, most probably due to the insufficient gravitational forces generated on earth (one has to wonder if future generations of soapmakers will ply their trade on Jupiter to take

advantage of increased gravity there). Further addition of water will move the kettle's composition into Region Q (the three phase neat-seat-lye region). Good separation can be found in this region however the addition of the "seat lye" phase increases the variability of the process and complicates processing. Best fitting occurs just over the border into Region N (the two phase neat-seat region). Here, terrene gravity can just overcome the molecular level forces and permit the neat soap and seat to separate. Addition of excessive water will result in relatively large amounts of seat and subsequent smaller kettle yields. A minimum of 8 hours will be required before the neat soap can be removed from the kettle, and longer times, if available, will provide a more consistent product.

Step 6A – Finishing an Oil Finish (OF) Kettle

At the point where an OF kettle is to be finished, it needs to have a chemical composition of no more than 0.7% NaCl and 32% water, the upper bound in Neat soap for these two components. Of course, the NaOH content will be much higher than the <0.1% levels required for Neat Soap. Typically, the settled OF Curd will have NaOH content in the 0.75 – 1% range. This excess NaOH content is removed by the addition of one or more of the following; a Fatty Acid, a Fat and/or Citric Acid. If a combination is desired, then add the Fat first because it is the most difficult to react and requires an excess of NaOH to saponify in a timely fashion. There is a great danger in adding too

much Fat if one is not patient to allow the saponification to be complete. Additionally, the fat added at this stage retains all of its glycerin, color and odor in the kettle, which could be a problem. A Fatty Acid reacts quickly, however most Fatty Acids have their own odor and color issues depending upon storage and handling, however there is no added glycerin at this step. Using Citric Acid to consume some or all of the excess NaOH is a recent development with surprising results. Although Citric Acid and NaOH produce Sodium Citrate, another electrolyte, the graining power of Sodium Citrate is quite weak and the kettle remains smooth. Additionally, there is a dramatic reduction in the viscosity of the finished Neat soap. This is of critical importance in the frequent occurrence of an incomplete settling during the final wash step. If indeed the settled Curd retains some lye (which is often the case), the moisture of the settled Curd will remain around 34%, thus when the Fat or Fatty Acid is added, the finished soap will have considerable Middle Soap content, making the soap unpumpable. Sodium Citrate levels in excess of 0.25% dramatically reduce the viscosity of the Neat/Middle Soap mixture well below even the most fluid properly composed Neat soaps. The danger lies in Sodium Citrate levels approaching 1%, which will result in a dried soap which will be difficult to press into a bar, being too crumbly. One needs to target Sodium Citrate levels at the 0.25% level to achieve pumpable viscosities in high moisture soaps without pressing problems in the finished Rice.

Secondary H₂O considerations

To accurately calculate the process defined above, a high level of accuracy and precision is required because the critical areas of maximum settling are relatively small. Traditional methods may overlook the following contributions to kettle soap H₂O.

Steam used for agitation and heating condenses into the kettle mass. This amount must be calculated by using the temperatures, heat capacities and heat of reactions of the various ingredients. Evaporation occurs during the settling process and must be considered. Finally, the kettle cools during settling and requires condensed steam to reheat.

Counter-current Illustration

The counter current nature of this process is now illustrated with a 4 kettle system using Figure 4. The processing steps are listed across the top; load, first wash, second wash, third wash, and finish. Loading of every kettle generates a neutralized or spent lye which is then sent to glycerol recovery. The wash lye removed from the first wash in kettle 1 goes into the loading of kettle 2. The wash lye removed from the second wash of kettle 1 goes into the first wash of kettle 2. The wash lye removed from the third wash in kettle 1 goes into the second wash of kettle 2. Kettles 2, 3 and 4 follow the same pattern. The seat generated during the finishing and the fitting of the

first kettle is used for the loading of the second kettle. The other seats are handled in the identical fashion. The counter-current flow becomes evident. The lines representing the production of soap go from left to right and the lines representing the flow of glycerol go from right to left.

Variations on a theme

There are many possible variations to the process outlined above. The process defined by Thomas Wood in Appendix A (1) of my prior writings adds the coconut oil during the first wash. Other options include graining the seat "off-line" and re-introducing this concentrated and washed seat into a washing step, thus loading on an empty kettle. One can also hold back a relatively large amount of NaOH during the loading step, thus saponifying only a fraction (say 85%) of the fats during the first step of the process. These variations, and others all have their features and benefits. However, all deal with the same phase diagram and the same concepts of graining and settling, thus all can be calculated in the same fashion.

THE MATHEMATICS OF A KETTLE OF SOAP

As in my prior work, I have used Microsoft Excel for the construction of my model. From 1982 to 2005, I wrote and modified the Kettle Soap Process Simulator (KSPS) using Excel and Excel's built-in macro programming language while under contract with Bradford

Soap, granting them exclusive use of the software. In 2005, long after my contract with Bradford expired, I decided that a total rewrite of the program was warranted. The KSPS was on Version 19 and had so many patches and modifications that it was very difficult to follow. Excel Version 11(2003) no longer fully supported the Excel Macro language. Excel's macro language migrated to Visual Basic for Applications (VBA), and offered much more power and flexibility. I also had developed a new strategy for loading and fitting a kettle which the KSPS could not support. I started with a blank spreadsheet in the newest version of Excel and created the Kettle Soap Process Controller (KSPC) which incorporates all of the newest technologies. Interested parties are welcome to a copy of the KSPC upon request.

Step 1 - Loading

In this section, I will attempt to explain my current approach to the kettle loading calculations. The same exact calculation scheme is valid for washing a kettle. Finishing a kettle is a different problem and will be discussed separately.

A kettle is loaded with the ingredients as outlined above. The total mass of the kettle is the sum of the ingredients:

$$M = M_f + M_c + M_b + M_y + M_r + M_w + M_t$$

We need to determine how much of each ingredient is required.

The kettle mass is also equal to the sum of its components:

$$M = M^s + M^\omega + M^g + M^d + M^h$$

The mass fraction of all of the components must equal 1:

$$1 = X^s + X^\omega + X^g + X^d + X^h$$

We also know that the mass of the kettle multiplied by the mass fraction of a component equals the mass of the component:

$$M^s = X^s M$$

$$M^\omega = X^\omega M$$

$$M^g = X^g M$$

$$M^d = X^d M$$

$$M^h = X^h M$$

In a similar fashion, each Mass Component has its own equation:

$$M^s = M^s_f + M^s_c + M^s_b + M^s_y + M^s_r + M^s_w + M^s_t$$

$$M^\omega = M^\omega_f + M^\omega_c + M^\omega_b + M^\omega_y + M^\omega_r + M^\omega_w + M^\omega_t$$

$$M^g = M^g_f + M^g_c + M^g_b + M^g_y + M^g_r + M^g_w + M^g_t$$

$$M^d = M^d_f + M^d_c + M^d_b + M^d_y + M^d_r + M^d_w + M^d_t$$

$$M^h = M^h_f + M^h_c + M^h_b + M^h_y + M^h_r + M^h_w + M^h_t$$

Combining equations gives us:

$$X^s M = M_f^s + M_c^s + M_b^s + M_y^s + M_r^s + M_w^s + M_t^s$$

$$X^\omega M = M_f^\omega + M_c^\omega + M_b^\omega + M_y^\omega + M_r^\omega + M_w^\omega + M_t^\omega$$

$$X^g M = M_f^g + M_c^g + M_b^g + M_y^g + M_r^g + M_w^g + M_t^g$$

$$X^d M = M_f^d + M_c^d + M_b^d + M_y^d + M_r^d + M_w^d + M_t^d$$

$$X^h M = M_f^h + M_c^h + M_b^h + M_y^h + M_r^h + M_w^h + M_t^h$$

We also know that the Mass of a Component in an Ingredient is equal to the Mass fraction of the Component in that Ingredient multiplied by the Mass of that Ingredient. Our 5 Mass Component equations then become:

$$X^s M = X_f^s M_f + X_c^s M_c + X_b^s M_b + X_y^s M_y + X_r^s M_r + X_w^s M_w + X_t^s M_t$$

$$X^\omega M = X_f^\omega M_f + X_c^\omega M_c + X_b^\omega M_b + X_y^\omega M_y + X_r^\omega M_r + X_w^\omega M_w + X_t^\omega M_t$$

$$X^g M = X_f^g M_f + X_c^g M_c + X_b^g M_b + X_y^g M_y + X_r^g M_r + X_w^g M_w + X_t^g M_t$$

$$X^d M = X_f^d M_f + X_c^d M_c + X_b^d M_b + X_y^d M_y + X_r^d M_r + X_w^d M_w + X_t^d M_t$$

$$X^h M = X_f^h M_f + X_c^h M_c + X_b^h M_b + X_y^h M_y + X_r^h M_r + X_w^h M_w + X_t^h M_t$$

This is getting a bit messy. However, there is some hope here. Many of these terms are Zero. For example, there is no Soap in Brine.

Many others are known. For example, the NaOH content of Caustic is typically 49.6%. Also, one typically knows the amount of Seat that is available for the kettle load. The mass fraction of H₂O in water and steam is 100%, so $X_w^\omega = X_t^\omega = 1$. The zero terms are eliminated, and the unknown values are bolded in our next set of equations:

$$X^s M = X_f^s \mathbf{M}_f + X_y^s \mathbf{M}_y + X_r^s M_r$$

$$X^\omega M = X_f^\omega \mathbf{M}_f + X_c^\omega \mathbf{M}_c + X_b^\omega \mathbf{M}_b + X_y^\omega \mathbf{M}_y + X_r^\omega M_r + \mathbf{M}_w + \mathbf{M}_t$$

$$X^g M = X_f^g \mathbf{M}_f + X_b^g \mathbf{M}_b + X_y^g \mathbf{M}_y + X_r^g M_r$$

$$X^d M = X_c^d \mathbf{M}_c + X_b^d \mathbf{M}_b + X_y^d \mathbf{M}_y + X_r^d M_r$$

$$X^h M = X_f^h \mathbf{M}_f + X_c^h \mathbf{M}_c + X_y^h \mathbf{M}_y + X_r^h M_r$$

We still have a ways to go, because we have only 5 equations, but we have 8 unknowns. As you know, we have to get this to a system where the number of equations equals the number of unknowns. We also want to keep this series of equations “Linear” so that matrix inversion techniques can be applied to achieve an exact solution.

We can perform an energy balance around the kettle to capture the mass of the steam that will condense as a function of the other ingredients:

$$0 = P_f (\bar{T} - T_f) M_f + P_c (\bar{T} - T_c) M_c + P_b (\bar{T} - T_b) M_b \\ + P_y (\bar{T} - T_y) M_y + P_r (\bar{T} - T_r) M_r$$

$$+P_w (\bar{T} - T_w) M_w + P_t (\bar{T} - T_t) M_t + \Gamma M_f$$

Depending upon the climate, the temperatures may fluctuate with the season. I have measured temperature fluctuations as great as 20°F in the northeast USA, and routinely adjust for it.

Here, the last term is the energy released during the saponification reaction. We now have 6 equations.

We revisit our mass fraction component summation equation for our 7th and final equation:

$$1 = X^s + X^\omega + X^g + X^d + X^h$$

Wait a minute! We have only 7 equations and 8 unknowns! We cannot solve this problem.

We actually can by solving 4 separate problems. Recall that we are adding recycled lye to this kettle. We first solve the problem of loading the kettle with the constraint of no lye added, or $M_y = 0$. This then gives us a linear system of 6 equations and 6 unknowns, something we can solve exactly with only one solution. After the solution is achieved, we have to confirm that indeed all of the ingredients are positive. You could imagine a situation where a very large and wet seat is used, resulting in a negative water addition. In this case, one has to reduce the amount of the seat until all ingredients are non-negative.

So we now have a solution in hand for a kettle loading with no added lye. That is solution #1.

Solution number 2 sets the caustic addition to zero, or $M_c = 0$. We again solve the problem. This solution could very well have a very large amount of lye added to the kettle forcing a negative water addition to achieve the correct loading target. This is of no consequence.

Solution number 3 sets the brine addition to zero, or $M_b = 0$. We again solve the problem. Again, this solution could very well have a very large amount of lye added to the kettle forcing a negative water addition to achieve the correct loading target. This too is of no consequence.

Solution number 4 sets the water addition to zero, or $M_w = 0$. We again solve the problem. Again, this solution could very well have a very large amount of lye added to the kettle forcing a negative caustic and/or brine addition to achieve the correct loading target. This too is of no consequence.

We now have 4 mathematically valid solutions to loading this kettle, although 3 of them may be physically impossible because of negative ingredient additions. Since we have valid solutions, any linear combination of these four solutions will also be a valid solution. In many cases we seek to consume as much lye as possible during the

loading stage. Of the three solutions that consume lye, there very well may exist one or more solutions where all ingredients are non-negative. In this unlikely occurrence, simply choose the solution with the largest lye consumption and your job is over. Most probably, all they lye containing solutions will have one or more negative ingredient. Pick the one with the least amount of lye, and perform a linear combination with the no-lye solution to find a solution that maximizes the lye addition with all other ingredients being non-negative.

If one desires to consume a fixed amount of lye which is less than the maximum calculated amount, then perform a linear combination of the two solutions weighted to achieve the desired addition of lye.

Fortunately, the power of Microsoft Excel and its associated Visual Basis for Applications permits the above series of calculations to occur in fractions of a second. This is the 'heart' of the KSPC and will be available to those who request it.

RATES OF ADDITION

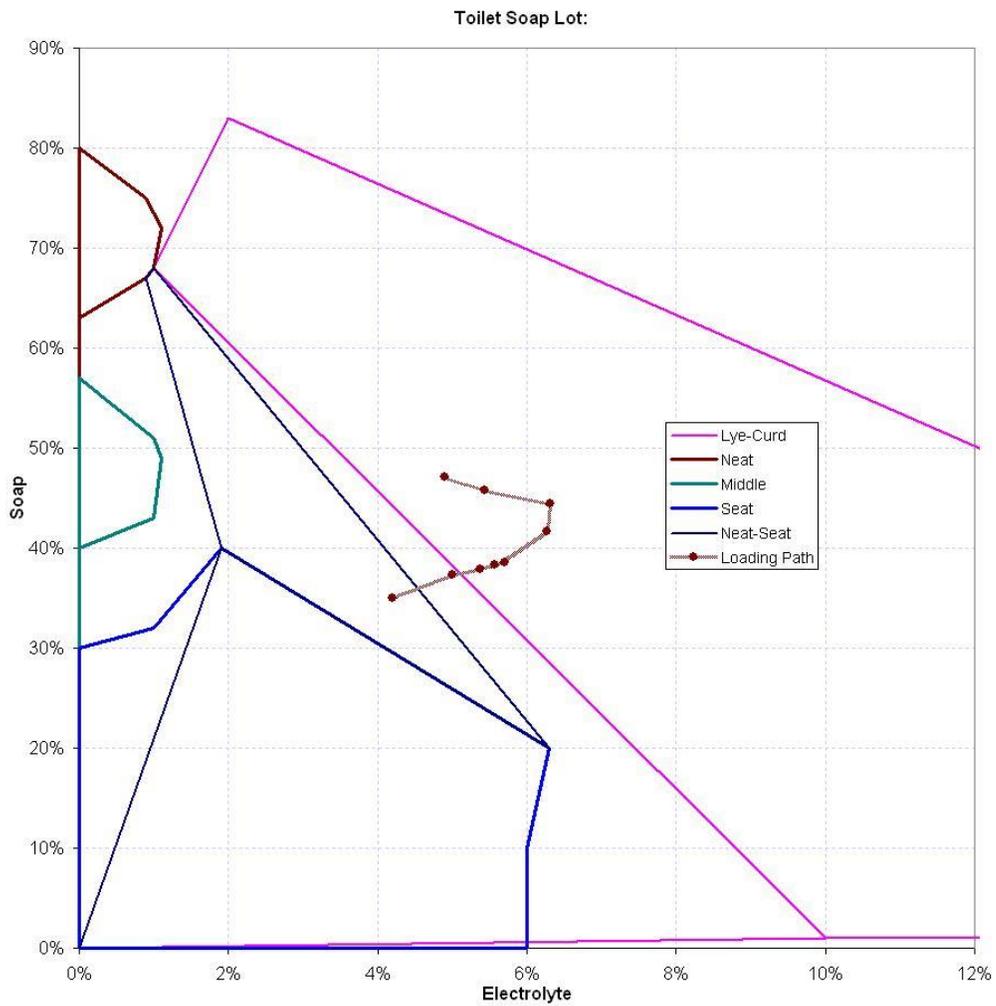
As discussed earlier, the success of the kettle is a strong function of maintaining the proper point on the phase diagram to assure maximum saponification. The loading target as defined is this maximum point of saponification. However, at the start of the loading process, the kettle's composition is identically the seat's

composition. In the simplified case of pre-blended fats, the first stage of loading is to move the kettle to the point of maximum saponification.

Fluctuating Fat Ratios

Often, a pre-blend tank is not available, forcing the soapmaker to add the fats either serially or sequentially. In the serial case, the tallow/coco ratio varies as the kettle's ingredients are charged. To maximize saponification in this case, one has to "hit a moving target" since the maximum saponification point is moving. Using the various "X" axis in the phase diagram of Figure 2, one can use a computer to predict this optimum point as a function of tallow/coco ratio, however, that calculation is quite involved.

I have solved this problem by providing myself with a graphical representation of the progression of the loading process. I have built my loading program to allow me to identify up to 15 different intermediate targets. I know the starting point of the load (the seat composition) and I know the end point of the load (the final loading target). I have found the best way to determine the intermediate loading targets is by trial and error, with a rendering of the path through the phase diagram imaged in an Excel chart. This illustration shows a kettle with a smooth loading path from seat to curd.

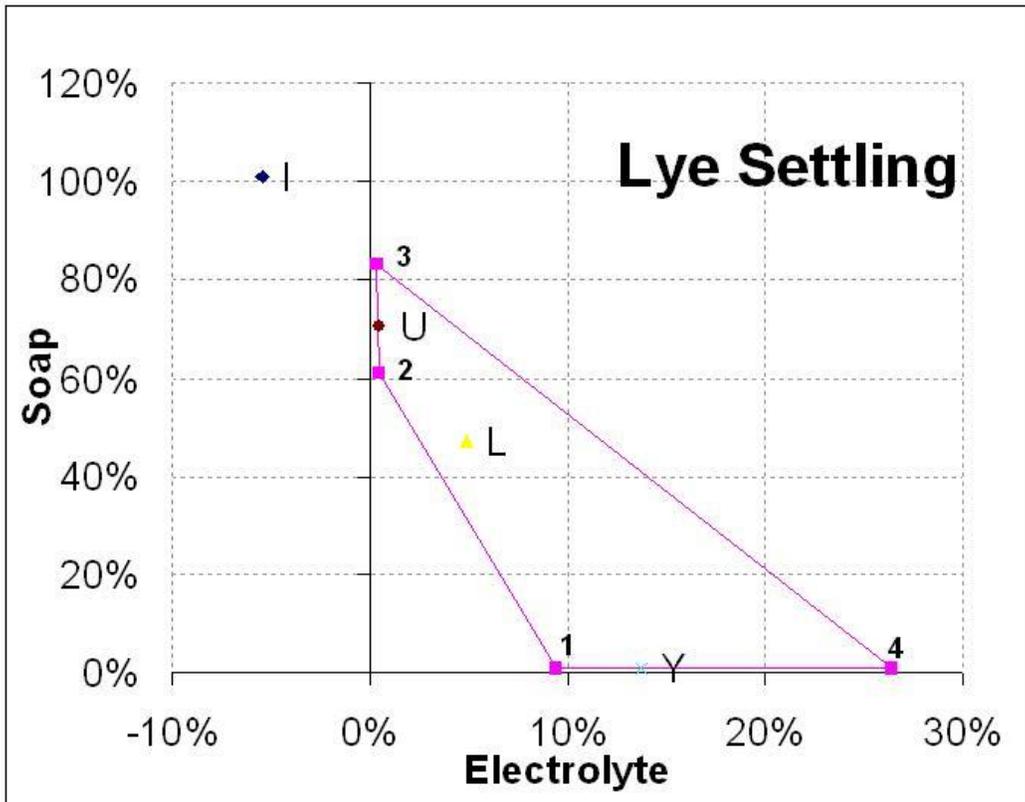


[Figure 5]

Kettle Settling

Okay, we have loaded a kettle. As we know, lye is dropping out. How much lye drops out, and what is its composition. Here is how

we figure this out. We approximate the lye-curd region as a quadrilateral.



(Figure 6)

Figure 6 shows a screen shot from the KSPC. This is a mathematical representation of the curd-lye region of the phase diagram. The X axis is percent total electrolyte; the Y axis is percent soap. The points 1,2,3 and 4 define this two phase region. L is the point where the kettle is loaded. Now here is where the math begins. First we define Point I which is the intercept of the two lines defined by line segments 1-2 and 3-4. We then draw a line through Points I and L.

This represents the phase diagram tie-line on which the loading point L resides. This tie line intercepts the line segment 2-3 at point U and intercepts the line segment 1-4 at point Y. Point U defines the composition of pure curd that evolves when the kettle fully settles. Point Y defines the composition of pure lye that evolves when the kettle fully settles. The relative mass of the curd and lye equals the relative length of the line segments defined by L-U and L-Y. These calculations follow the rules of phase diagram theory as outlined in any book on the topic. All of the math that defines this is simple algebra, a far superior approach than in my previous work (which nobody understood).

Our work is not yet done. The curd and lye does not fully separate. I define a “Lye Drop Factor” which is a value from 0 to 1 to define what fraction of the lye actually drops out of a kettle. This Lye Drop Factor varies with the loading target and is typically between 0.78 and 0.9, meaning 78% to 90% of the total available lye will be removed from the kettle.

We also have to determine the amount of NaOH and NaCl in the lye and curd phases. What I have found is that the ratio of NaOH to NaCl stays constant during the settling. This is also true for the Water to Glycerin ratio.

Of course, the kettle has cooled during this process. Steam must be used to reheat the kettle for the next processing step. This steam condenses and increases the water content of the kettle. This must be determined to maintain an accurate record of the kettle contents.

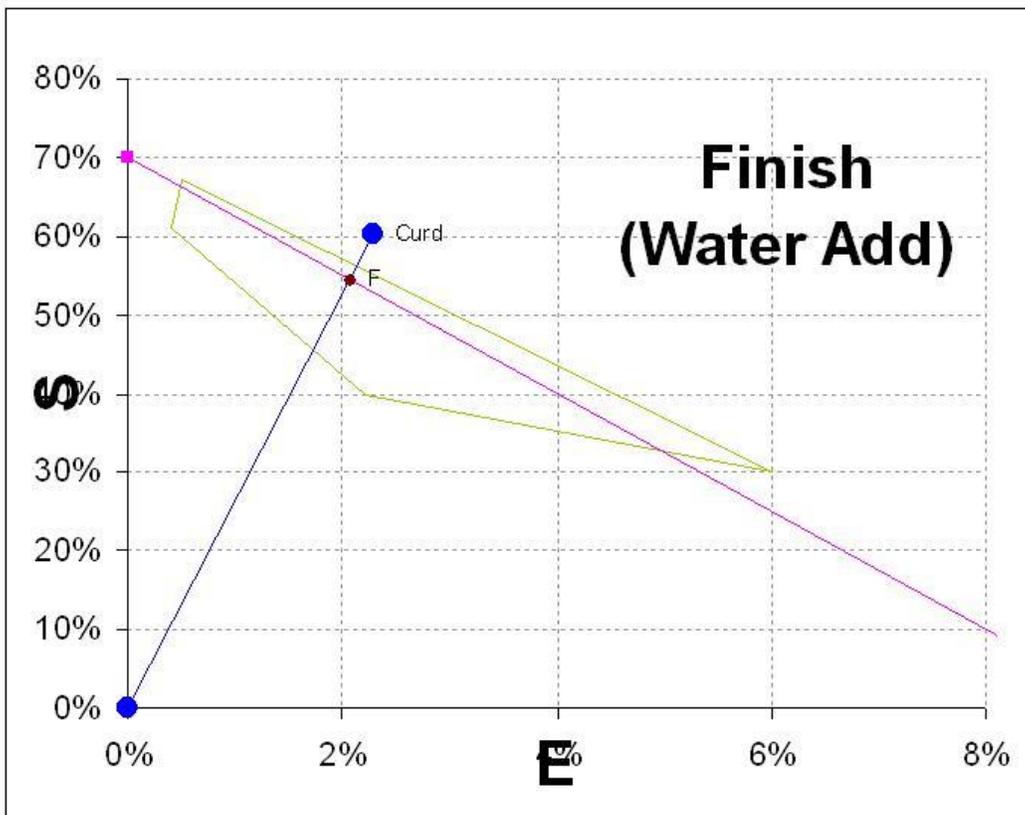
This summarizes all of the aspects of loading and drawing lye from a kettle. Obviously, someone attempting to implement this technology has a lot of work ahead of him or her. Hopefully, this effort provides some useful guidance. As mentioned earlier, washing a kettle follows the exact same scheme. Fitting a kettle is a different problem.

Kettle Fitting

Unlike loading or washing a kettle, fitting a kettle involves addition of only water to move the kettle from the curd-lye region on the phase diagram to the neat-seat region. Consider the phase diagram.

Addition of water to a kettle is represented on the phase diagram as moving towards the origin. Recall that the origin is 100% solvent, 0% soap and 0% electrolyte. Also recall that the key to successfully settling a kettle between two phases (curd-lye or neat-seat) is strategic placement on the phase diagram. During the loading and washing steps, a specific point on the phase diagram is specified and achievable because two or three components (soap, solvent, electrolyte) are being added. During the fitting step, only one component is being added (water), so in most cases it is impossible to

achieve an exact point on the phase diagram. One can, however, identify the desired line segment that represents the ideal tie line to achieve optimum neat-seat settling. This is exactly what is done.



(Figure 7 here)

Figure 7 is from the KSPC and illustrates. The composition of a Curd is identified on this graph as well as a quadrilateral representation of the neat-seat region. Infinite dilution of the kettle with water is represented by a line segment drawn from the curd to the origin. The target line segment is illustrated as well. It is simple algebra to

calculate the interception of the line to the origin and the ideal tie line. This interception point is the point where the kettle is to be fitted.

Once this fitting point is identified, the software then determines the amount of water to be added to the kettle to achieve that point. Since this is a very exact measurement, steam adjustments have to be made. There are two steam adjustments to consider. First, there is the amount of steam required to bring the added water to a boil. Second, there is a substantial amount of steam that condenses while heating the kettle. Once the kettle is boiling, the additional steam that is injected for continued agitation simply passes through the kettle. There is a small amount of steam that continues to condense while the kettle is being mixed. This is due to the fact that the kettle is not perfectly insulated and some heat is lost through the kettle sides and bottom.

Oil Finish

This new and novel approach requires careful manipulation of the kettle. Again, the kettle is loaded and washed in the traditional fashion, however the wash targets are skewed to include a significantly greater amount of free NaOH and much less NaCl. Therefore, after the final lye is removed from the final wash, the total NaCl content of the kettle equals the desired NaCl content of the neat

soap. Therefore, there is a extremely high NaOH content which must be neutralized.

A well behaved OF kettle will have between 0.75% and 1.0% NaOH content. As mentioned earlier, it is essential to avoid a high solvent content in the curd or else Middle Soap will exist and make the resultant Neat-Middle mixture too viscous to pump. For a 85/15 Palm/Coco soap I have found a wash target to be 49.9% soap, 2.27% NaOH and 1.53% NaCl. This will generate a lye composed of 7.23% NaOH and 4.85% NaCl. Removing 80% of the lye (remember, we are on Earth, not Jupiter) has a resulting curd of 64.7% soap, 0.76% NaOH and 0.51% NaCl, leaving the total solvent level at 33.9%. Remember, the total solvent level is the sum of the water and glycerin. The glycerin content is a partial function of the amount of recycled materials added in prior steps and can 'float', so the total solvent level should be the focus of attention.

Again, I must caution that attempting to saponify fats or oils to consume this excess NaOH is difficult and time consuming. However, one could reduce add some Fat and/or Oil to the kettle to consume a fraction of the excess NaOH. I have found that a minimum excess of 0.5% NaOH should be maintained to assure any fat or oil added at this step is completely saponified.

Once the 0.5% NaOH level is achieved, we are left with two options to neutralize the balance. I have found that using just fatty acids sometimes results in stiff soap which is difficult if not impossible to pump. However, neutralizing ½ of the remaining NaOH with Citric Acid actually substantially lowers the viscosity of the neat soap and is highly recommended. One has to do some trials to determine the maximum amount of citric acid a particular formula can tolerate and still maintain proper physical properties of the finished bar. Levels as low as 0.1% Sodium Citrate have a tremendous benefit to the neat soap viscosity without impacting the final bar.

FUTURE PLANS

In short, I have no future plans to for any major developments to this program. Bradford Soap continues to use the KSPC, but my efforts there are limited to maintaining what is a very mature process. With negative growth in the USA for bar soap products there is little if any financial incentives to do further development. At this writing, crude oil has topped \$142 US per barrel with tallow and coconut oil prices at all time highs. Liquid soap market share continues to climb. All of these factors combine to paint a bleak future for bar soap and in particular kettle soap in the USA.

I have had very limited success in exporting my technologies to other countries. Despite the (in my mind at least) obvious savings in the

incorporating of this technology into existing kettle soap operations, companies outside of the USA are unwilling or unable to pay me comparable amounts of compensation I am currently receiving from the pharmaceutical and telecommunications industries. For this reason I am willing to provide copies of the KSPC to anyone who requests it. Please contact me directly.

ACKNOWLEDGMENTS

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