Comment on the Australian Government's position on
Proposed Fuel Quality Standard for Fuel Grade Ethanol – July 2005

Lemon Tree Ethanol & Wells Enterprises International

Thank you for this opportunity to comment on your document "SETTING NATIONAL FUEL QUALITY STANDARDS - Proposed Fuel Quality Standard for Fuel Grade Ethanol, July 2005." I am commenting on behalf of Lemon Tree Ethanol, a proposed project in Millmerran, Qld and for my consulting business, WEI Pty Ltd.

On page 4 I draw your attention to the last sentence in the first paragraph of Section 2, which reads "It is proposed that the standard will apply to neat ethanol (E100) for use as blend stock with petrol up to 10% volume." This sets an important frame work for the parameters; for example, one might look differently at E100 being used to make E85 for fuel flexible vehicles, for there the properties are not diluted by 9 parts petrol to one part ethanol, they are only diluted 1.5 parts petrol to 8.5 parts ethanol, thus the concentration of critical components is even more important. In fact, you make this point in the 5th paragraph

I do not have a copy of US ASTM D4806-04a before me, but I do have a summary of the specifications found in D4906 (for denatured ethanol only) dated May of 2002, so there may have been changes since I left the USA that I have not seen. I apologize in advance if this causes error on my part, but I suspect that little has changed. I am guessing that the -04a specification must be for E100 (no denaturant), something I do not have.

I will now run through the specs as seen in Table 1 and elaborated upon in Table 2.

Ethanol content. ASTM distinguishes between "ethanol" and "fuel grade ethanol." The former is the specific chemical substance ethanol, also known as ethyl alcohol and includes nothing else. By fuel grade ethanol they mean that substance (mixture) produced in a fuel grade ethanol plant which contains not only the species "ethanol" but also limited amounts of water, methanol, acid-like substances (as measured by titration or pHe electrodes) and that nebulous group of chemicals known as fusel oils. These are mostly higher isomeric alcohols in the C3 to C5 range, but can also include traces of light ends such as ethyl acetate. These are clean burning chemicals, desirable for inclusion in petrol, which actually improve the water tolerance and joule-content of ethanol in petrol, and so are allowed to be present in the natural amounts in which they are produced. Indeed, fuel ethanol plants usually have no means of cleanly separating or getting rid of them. It is important to note that no extra fusels may be added, only that which is produced along with the ethanol by metabolic action of yeast.

How much is permitted to ensure no one is dumping extra chemicals in similar to or the same as the fusels? While it is not spelled out specifically in the text section of D4806 - 99 (I assume this is from the year 1999), you can impute the amount from the section entitled 4. Performance Requirements. There you can see that the content of the specific chemical "ethanol" must be at least 92.1% in the denatured ethanol, and one assumes this to be at the highest allowed addition of denaturant, 4.76%. Adding up all the ingredients in this section (percentage, or parts per 100 parts) one gets ethanol 92.1, methanol 0.5, water 1.0, and denaturant (gasoline or petrol) 4.76. This only adds up to 98.36, so the rest (1.64) must be the organic fusels. Now you can re-normalize and come up with the composition of the major elements in undenatured fuel grade ethanol; that is, ethanol 96.7, methanol 0.52, water 1.05, and fusels 1.72. All these taken together are considered to be undenatured "fuel grade ethanol."

I do not think it is a problem to limit non-ethanol and methanol organics to 1.7% by volume, but it would be hard to quantify them because they are a diverse lot. Instead, I think it is easier to require that the ethanol content as the species ethanol be whatever number is appropriate for the amount of denaturant

present. If the fuel grade ethanol (E100) is undenatured, then something around 96.5% minimum would be valid and realistic. I will calculate what it should be in the discussion herein on denaturants, which is further on.

Methanol content. I see in your comments in Table 2 that the lower value of 0.1% (versus 0.5% methanol in D4806) is based on your judgement of the corrosive nature of methanol and the ability of Australian producers to make this grade. I would caution you that current producers move the majority of their product into the industrial (includes beverage and pharmaceutical) markets where low methanol is required, but the fuel grade ethanol plants of tomorrow in Australia will not have any extra distillation capacity to get the methanol this low. It is not a simple or inexpensive task. Nor, in my opinion as a fuel scientist, do they need to. The methanol molecules are so far apart at 0.5% that they cannot "gang up" on metallic surfaces to do any damage. Plus there is the cosolvent effect of the ethanol surrounding the methanol to hold it away from harm.

I would point out that the "du Pont" and the "ARCO" waivers to the Clean Air Act were in effect for many years allowing methanol up to 5% to be blended with a suitable higher alcohol cosolvent of at least 2.5% content, such as methanol, isobutanol, or tertiary-butanol (also known as t-butyl alcohol, TBA). Many thousands of millions of gallons of these fuels were sold (I myself did this kind of blending in the mid 1980s) and the ARCO company moved gasoline-methanol-TBA blends through the pipelines in Pennsylvania for years. They would probably still be doing it if they had not discovered they could dehydrate TBA to isobutylene, and react that with methanol to make MTBE. The rest, as they say, is history.

In conclusion, I will say that you will unnecessarily disadvantage future Australian ethanol producers with a spec this low. All the grain technology, for example, will be based on the American standard which distils to D4806 specification. In my opinion, 0.5% is adequate, even for the denatured product. Methanol is not corrosive in the sense that dilute sulfuric acid is; rather, in concentrated states, it will attack selected metals such as zinc and high-copper aluminum alloys, and in concentrated states it will swell elastomers not designed to handle it (some rubber hoses, especially older non-fluorinated ones). At 0.5%, there is not enough methanol to swell and harm elastomers, even if the molecules permeate the interstices of the polymer matrix.

Non-volatile matter. I have no basis for comparison with this as it is not part of D4806, but I can see that it might be important to control this at some level. I have heard of ethanol getting contaminated by non-volatile foreign matter left in poorly-cleaned vessels during transit, or "fines" from molecular sieve beads carrying over. I concur this should be capped at some level, but I do not know if this is too stringent or lenient. Technically, there should be none because it is distilled and filtered. I would once again hesitate judging fuel grade ethanol quality by current Australian capabilities because it is geared to industrial, even at Manildra.

Water content. This level is fine. If the petrol were bone-dry (which it will nearly be) and the only source of water was the incoming ethanol, blending to E10 would result in a water level of 0.1%. It is my experience that E10 can hold nearly five times that amount of water, so the E10 will actually help keep the fuel system dry, and it is water that does most of the corrosive damage in an engine.

Denaturant content. These min and max levels seem fine to me. I might add some background from the USA to give you a feel for the experience there.

As in Australia, it is the Treasury Departed that controls the amount of denaturant required, in this case by the Bureau of Alcohol, Tobacco, and Firearms (BATF), in an effort to prevent avoidance of tax payment on potable alcohol. For as long as anyone can remember, the formulas have been at least two gallons and not more than five gallons of gasoline (petrol) per every 100 gallons of ethanol. Thus, you see the source of the odd amounts seen in D4806 of (100x2)/102 = 1.96% and (100x5)/105 = 4.76% as the denaturant range. BATF also specify that for fuel grade ethanol, the denaturant need not be gasoline that is otherwise ready for sale at a service station (finished gasoline), instead it can be any mixture of hydrocarbons in the gasoline boiling range , or even pure components such as toluene just so long as they cannot be separated

by simple distillation once added. The reason this has been so important is that the liquid associated with natural gas production, called natural gasoline, sells for considerably less than refined gasoline from a refinery, and it is common in the Midwestern USA. This material is also more environmentally acceptable because of course it contains no toxic aromatics or olefins, and being primarily mixed alkanes (aliphatics) the ozone-forming potential is lower than with gasoline.

Accordingly, I suggest you liaise with BATF and US Customs (Customs also get involved for international shipments in or out) and see which denaturants are suitable for fuel grade ethanol use. I do not think corrosion inhibitors by themselves are adequate unless they contain something that azeotropes with ethanol or boils so closely it cannot be separated by distillation.

As promised, here are the (pure) ethanol contents expected at 1 and 5 vol% denaturant starting with 96.7% in undenatured fuel grade. First, one must calculate how much denaturant must be added to make 1% and 5% levels. Simple one-variable equations do the job: $(x)/(100+x) = 0.01$, then $x = 1.01$; similarly, $(y)/(100+y) = 0.05$, $y = 5.263$. Said another way, for every 100 litres of undenatured fuel grade ethanol, you must add 1.01 litres denaturant to get a final mixture at 1.0% denaturant. Similarly, for every 100 litres of undenatured fuel grade ethanol, you must add 5.236 litres of denaturant to arrive at 5.0% denaturant in the mixture. I think you can see why BATF choose to make it more user friendly by saying 5 gallons to 100 gallons, especially in the days before in-line blenders. These days, the instruments can be calibrated and it will not be a problem.

Now we can calculate the pure ethanol percentage in the denatured alcohol mixture; that is, the concentration of the particular alcohol "ethanol." For 1% denaturant it is $(0.99)(96.7) + (0.01)(0) = 95.73\%$ and for 5% it is $(0.95)(96.7) + (0.05)(0) = 91.86\%$.

Copper content. Fine as stated.

Acidity. Fine as stated. You mention a future EU standard, is it going to 0.007 as well? (you do not need to respond) If you are sure they are doing this, okay, but I would not rely on something not yet in place. ASTM covers it well and has stood the test of time and large usage.

Appearance. Fine as stated.

Sulphur. Use of California standards seems OK at first glance, but remember that Australia has no extremes of air pollution the way California does. I would pay particular attention to what oil companies say on this point. It is improbable that ethanol will contain much if any sulfur, and in any case it will always be lower than what is delivered in the 90% fraction, petrol. Still, you do not want to add more. I think that since neither mainstream America nor Europe address this, it would be prudent for Australia to be silent on this as well until some nation that blends to a significant level such as the US or EU make a pronouncement. It just seems a little forward for Australia to jump ahead on this, particularly since petrol is the principal offender.

Phosphorus. Same problem with basing it on something in the EU that is proposed but not yet in. There is no history I know of in controlling this in ethanol, no yardstick for ethanol producers to benchmark their own analytical work. I think this is premature, even more so than sulfur.

Page 7. Moving on, I see now on page 7 that you intend for the standard to apply to denatured fuel ethanol, much as D4806 is. That is fine, but provision must be made for those who ship ethanol in bond "clear" without denaturants. Producers far inland will do this where they can and it will be up to the buyer to add denaturant at a refinery or storage depot before delivery into a tank.

So basically, having read this more carefully, my comments on undenatured fuel ethanol are just an academic exercise. I hope that you might take some value from it. I would also point out that it is not to hard to make the point of excise payment as that point at which the product leaves bond and denaturant is added (or E10 is made if the E100 is clear). That way, product can move around to where it is needed on a sort of moving-storage-tank basis without yet attracting excise. Also, let's say someone like BP takes

ethanol from Lemon Tree undenatured and moves it straight into the Brisbane refinery. If petrol is more expensive than ethanol, then why would BP not use the full 10% ethanol as undenatured rather than dilute it with 1% denaturant and then use that product as the blending agent within their own refinery? They should have the option to just make a 90/10 blend with petrol and E100 (undenatured) and at that point the excise gets sorted out.

It seems in the next subsection on denaturants that you are taking the easy way out and not necessarily considering market forces that might allow things like "natural gasoline" as is done in the USA (see my previous explanation). Thus you are giving refiners or finished fuel importers a monopoly and excluding some enterprising Australians who might take advantage of those liquids associated with natural gas production that are very clean burning, in the petrol boiling range, render the ethanol permanently unfair for human consumption, and environmentally benign. PNG might be a good source for these products, as well as Western Australia, and help to strengthen that region as opposed to sending more of our money (however indirectly) to the Middle East.

Regarding corrosion inhibitors (bottom page 7 and top of 8), that is all well and good except that major refiners frequently have their own proprietary additive package that they want to use and will not be happy if the ethanol seller routinely uses a competitor's product. Once it is in the storage tank at the ethanol plant, it is "contaminated" forever.

I am confused by two statements at the very end of this section at the top of page 8. (1) You state that ATO permits corrosion inhibitors to perform the role as denaturants. While the ethanol may now be undrinkable after this addition, have they considered whether the ethanol can be re-made into potable product by simple distillation? Most of these inhibitors are comprised of high boilers or even non-boiling high molecular weight polymers and thus could be left behind in distillation. This is just something for you to think about. (2) The other point is the point you make where a customer uses straight E100 (so it is possible???) and adds corrosion inhibitor (fine) and / or ignition enhancer. These "ignition enhancers" would never be used in making E10 in petrol, they are used for e-diesel, where the high octane of ethanol must be balanced with small amounts of what amounts to pressure sensitive"explosive" (nitrates or peroxides or similar products) to make the fuel have a higher cetane number so it will light-off during piston compression. I think you may have mixed apples and oranges here (diesel and petrol applications). Maybe you did it on purpose, I will read on and see.

Page 8. I have no comment on the Test methods as I am not up to speed on the latest analytical thinking. I can only say that, to the extent you adhere to the latest version of the ASTM procedures found in D4806, you will be fine.

I have a problem with a sentence in the next section entitled Ethanol petrol blends. You state that the E10 will have to meet the same standard as clear (non-oxygenated, Determination 2001) petrol after the 10% ethanol is put in. Rather, I think you should say that so long as the ethanol meets its separate standard, and the all-hydrocarbon blendstock meets its standard, then the resultant E10 blend is OK. Now that I think about this some more, even that is restrictive, because, as happens most of the time in the USA in the reformulated gasoline areas, the gasoline used to make E5.5 to E10, prior to ethanol addition, might not meet the spec in certain ways, especially if the spec includes such things as octane and volatility issues. These basestocks are called suboctane, RBOB, etc. in various markets and are usually not suitable for sale in the intended market for various reasons, especially low octane until the ethanol is added.

The ethanol, when it is added, complements the base petrol and fills in the final octane and volatility, plus it adjusts the Driveability Index, etc. Not only that, some States (in the USA and Queensland, for example) allow that if the Reid vapour pressure (Rvp, pressure exerted in a sealed canister at 100 degrees F) is on spec before the ethanol is added, it can to rise to what it will after the ethanol is added. Now let us go on and see what you have said next before I comment further.

By the way, I agree with your assessment and actions should E85 present itself in Australia at a future date.

Page 9 and 10, volatility. Simply stated, this is a specification for E100 and I think you should be silent on the issue of all volatility determinations, whether Rvp , FVI, distillation curve, whatever. I think this is a State issue and not federal, but that is my opinion. Also, I have commented in the past on FVI and find it of no real value. As for the distillation curve, of course it will look completely different in E10, but this is an E100 spec, where the curve is almost be a flat line around the boiling point of ethanol, with some tails for light and heavy ends and the denaturant. This whole issue is wrapped around hydrogen bonding, approach distance of polar neighbours = concentration of ethanol, so on and so forth, and strays from the issue of E100, which is what it is. On the other hand, petrol can vary quite a bit and so the Rvp response of fuel ethanol when it is blended into various grades of petrol will also vary. If you would like a (boring) lecture of Rvp and ethanol, I can provide this, but it has no bearing on E100 specifications. Perhaps you could put a restriction on folks using straight butane for denaturant or something like that. A performance test would be better, such that E100 (denatured) have a starting Rvp of no more than so and so, but remember this: it is the separation of the polar ethanol molecules (widening of the hydrogen-bonding distances, lessening electrical attraction by the inverse of the square of the distance) that give rise to the odd phenomena seen in blends up to 10%. Also remember this, no matter what the denaturant is, at a max of 5% in E100 it will be at a max of 0.5% in E10 so therefore will exert very little influence in finished petrol. I do not have enough room here to discuss all this, let me know if you want to know more.

I would say this: in modern fuel injected cars with submerged fuel pumps, vapour lock is impossible because the sending unit is wet (in the tank) and pushing the fuel forward, plus it is always under pressure. Carburetted cars are just about gone, and who knows, maybe these have fuel wet pumps as well these days. A much more serious issue is using fuels that are too low in volatility in an attempt to limit evaporative emissions (don't forget, you have a carbon canister for this) in a particular airshed. These are distinguished in the USA by excessive highness in the DI, which results in "fruitless cranks" in a "cold" engine (even on an ambiently hot day) which in turn spews out raw petrol into the atmosphere. These same cars will also show poor driveability during the early portion of the driving cycle until the engine comes to equilibrium temperatures. Call me if you want to discuss this as well, I have data to back this.

I see you mention the BOB in the last part of this section, but realize that its lower volatility (only necessary in the most polluted airsheds, I doubt Australia has anything as bad as Los Angeles or Houston) may put it out of spec seasonally as too low, so you might have to reconsider your language to allow these BOBs.

Page 10. Oddly, synthetic ethanol from fossil hydrocarbons (ranging from methane to ethylene to coal) also have something like fusel oils and they are present in about the same amount, but they contain some real "baddies" such as crotonaldehyde, a toxic lachrymator which also polymerizes to gums! Brazil required that South African ethanol made from coal (Sasol) have this removed before shipment during periods of ethanol shortage in Brazil (it has happened). More importantly, one should take a holistic view of government policy and realize that the major intent of the E10 movement is the utilization of non-fossil, indigenous (domestic) agricultural or forestry products in making ethanol for Australian petrol. This is emphasized in the excise treatment for these products, and it is probably codified in other ways I do not know about.

I would say that an audit trail is easier, but there have been abuses in the US before where only carbon-dating was suitable to detect the fraud. Obviously, the carbon dioxide would have been fixed only recently into sugar or starch or cellulose with renewable resources, while the rest is, well, fossil and old.

I see the rest of the document is informational and not germane to E100 for making E10 in petrol, so I will end my comments