

Separating Azeotropes using Light and Nanoparticles

M.J. den Exter
F.O Lenzman
M. Saric
J.B.J. Veldhuis

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Abstract

The azeotrope ethanol/water could not be broken by the use of nano-particles that are heated by light. Several insufficiently quantified parameters hampered exact mimicking of a reported breaking of the same azeotrope in the open literature.

Normal rectification was observed which might also be the case in the aforementioned reported experiment.

It can, however, not for 100% be excluded that the reported phenomenon of breaking an azeotrope with nanoparticles and light exists since many parameters during distillation may be of influence.

A rough preliminary economic evaluation, in case of positive findings, shows unfavourable economics compared to the use of adsorbents such as zeolites.

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Summary

Breaking of the ethanol/water azeotrope by light and gold-coated nano-particles, as reported in literature, could not be reproduced. Parameters such as wave length travel distance, actual power input, temperature of the bulk liquid at the moment of collecting condensate, influence of stabilizers on the surface of the particles and the influence of agglomeration of the particles hamper actual mimicking the reported data. It was also found that normal rectification can take place during distillation and that this may very well also be the case in the reported experiment in the open literature. This makes the actual existence of breaking an azeotrope with nanoparticles and light questionable. It can, however, not for 100% be excluded that such a phenomenon exists since all parameters may influence each other.

A rough preliminary economic evaluation shows that, compared to complete dehydration of ethanol above the azeotropical point, the use of gold-coated nanoshells is strongly uneconomical.

It is therefore recommended not to further pursue investigations in this area.

1

Introduction/background

In 2012, an article was published in American Chemical Society- Nano.(Neumann 2012). The authors were able to make steam of 150°C directly from ice water using concentrated sunlight, with the aid of nanoparticles dispersed in the ice water. A local highly-non equilibrium situation is preventing the steam bubbles formed to cool down and heat up the ice water. This phenomena is very interesting from a fundamental point of view, but converting solar heat in steam of this temperature is not a fundamental difference from other direct sunlight applications.

A second application from the article is the use of the same combination of sunlight and nanoparticles to affect the vapour-liquid equilibrium composition to break azeotropes. Some mixtures, like alcohol and water, cannot be separated to high purities unless expensive and energy consuming entrainment techniques are used. The authors claim that they can overcome the normal equilibrium restrictions. Instead of sunlight also artificial light or electromagnetic radiation source can be used. This could potentially lead to less energy consumption in distillation since the use of an entrainer could be prevented. The azeotrope composition of ethanol/water and N-propanol/water, the mixtures that will be investigated, are shown in Figure 1:

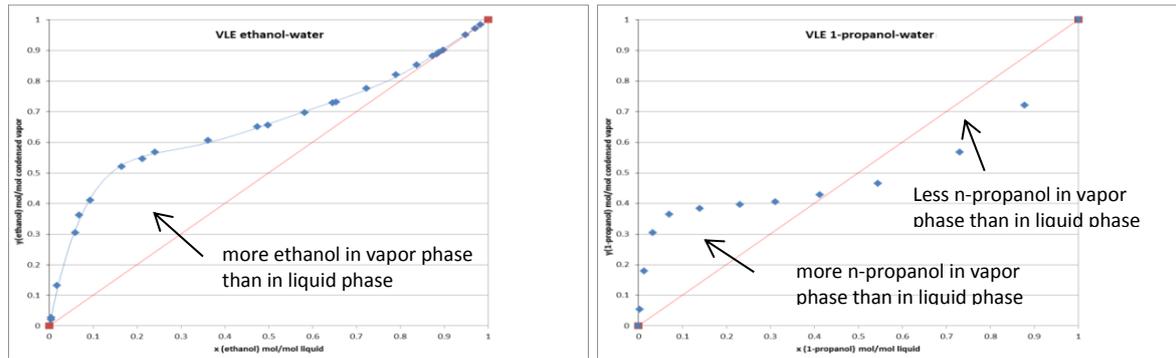


Figure 1: Vapour-liquid equilibrium compositions for water/ethanol and water/n-propanol

For azeotrope distillations, an entrainer is used that has to be recovered which is energy inefficient. Both normal distillation and azeotropic distillation are shown in Figure 2:

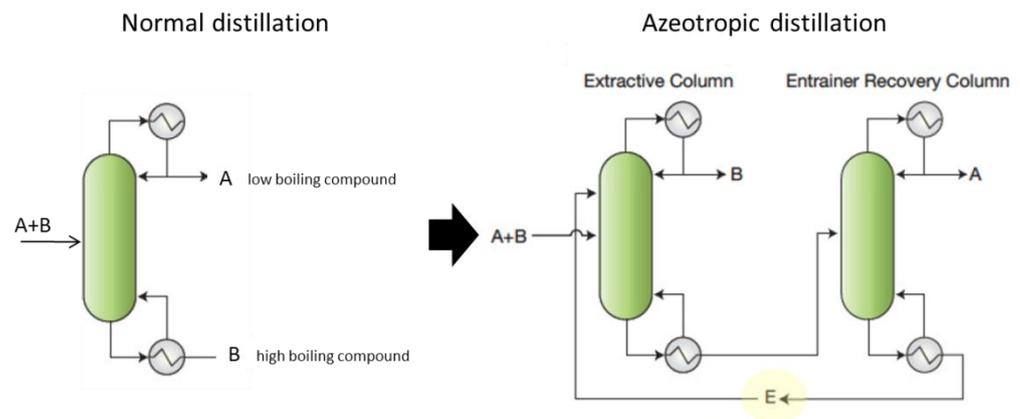


Figure 2: normal and azeotropic distillation

It is envisaged, if the principle of selective heating of particles by light breaks an azeotrope, to design a distillation that comprises of a normal distillation column and a separate column which breaks the azeotrope, as shown in the following figure:

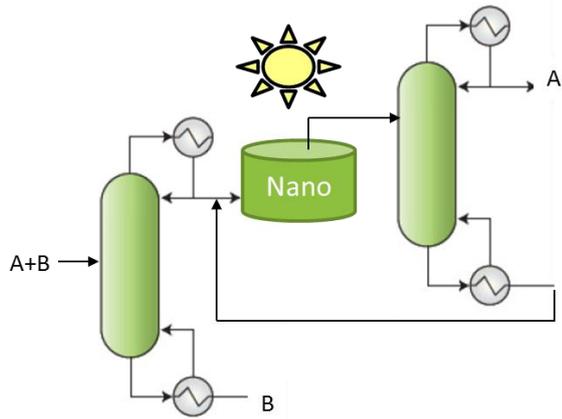


Figure 3: distillation column equipped with a unit comprising nano-particles and light

Project aim:

The aim of this project is to identify the claim of breaking azeotropes with light and nanoparticles since the errors in the measurements, as reported, are high and from that point of view, the statement of breaking azeotropes may not be true. For this, mimicking the reported experiments with less experimental errors is the tool to verify the reported results. In the project, both expertise of ECN Solar Energy and ECN Biomass and Energy Efficiency group are combined. Together with verifying the reported results, ideas on how to proceed with this possible new way of distillation in case of positive confirmation will be developed and recommendations given for further continuation together with industry. A theoretical assessment will be made of relevant phenomena and possible working mechanism(s) and consequences for practical application, to back-up the recommendations.

2

Experimental setup

A commercial VLE-setup is not possible since this would consume the entire project budget. Therefore, a home-made setup was developed. The experimental setup consists of a simple distillation setup that has been dimensioned in such a way that a 20 ml feed can be handled, conform the distillation as reported in literature, and minimized space and possible reflux. A lamp with a Fresnel lens is focussing the light onto the feed. During the distillation, the temperature can be measured and small samples can be taken from the condensate for determination of the composition. A commercial VLE-setup is not possible since this would consume the entire project budget.

Two types of lamps have been obtained:

- A normal white-light lamp with electrical power of 100W and 1000W;
- A led-based flat-plate lamp with a wavelength output of 630 nm which is not optimal considering the adsorption maximum of 20 nm gold at 520 nm. A new led-based lamp with 520 nm output is considered but needs to be made.

Since the exact power input as used in the article is unknown (communication with the author has not resulted in more information), while the publisher used normal sun-light and a Fresnel lens, also normal sunlight and a Fresnel lens was considered if the lamps do not provide sufficient power input into the feed volume. A schematic view of the initial setup equipped with a flat-plate led-based lamp is shown in Figure 4.

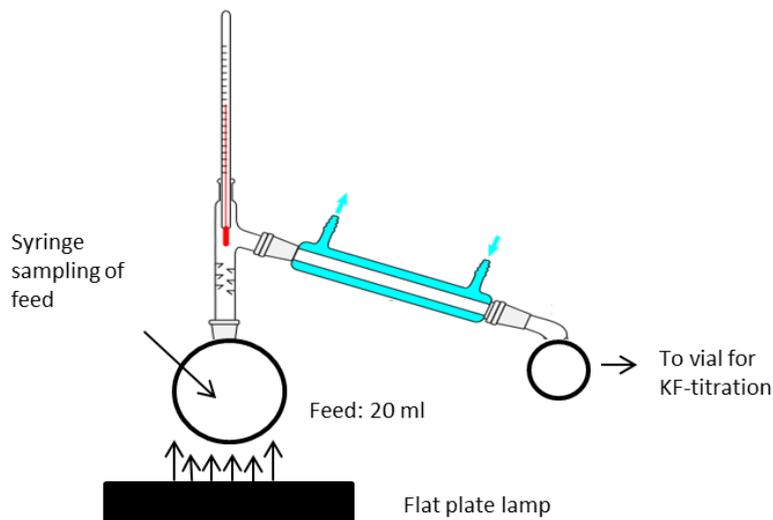


Figure 4: experimental distillation setup

In order to decrease the travel distance of the light through the bulb and to be able to cool (as was also done with ice in a double walled glass vessel in the reported experiment), a double walled glass vessel was developed at ECN as well.

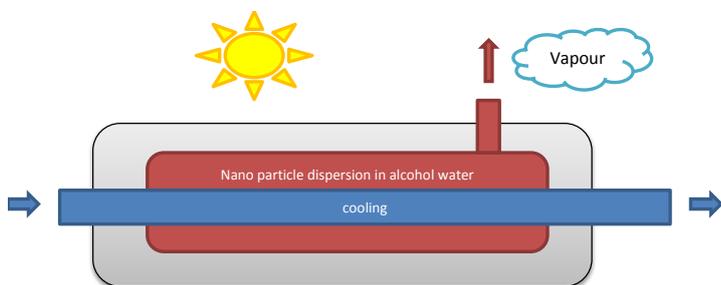


Figure 5: actual double walled glass vessel

Picture from top of reactor and schematic layout: the grey outer tube has low pressure inside. The red area contains the nanoparticles and liquid (approximately half the volume is filled) and the blue inner tube provides the heating or cooling through a connected thermostat (not shown).

It has to be noted that the project description specifically states that the use of sunlight is not considered, only lamps. However, if with lamps no distillation occurs because of insufficient power, the use of sunlight combined with a Fresnel lens cannot be avoided.

The glass bulb consists of Duran glass with a transparency of 90% for normal sun light.

For analysis of the condensate, Karl-Fisher titration (KF) was selected as analysis tool. Gas chromatography (GC) suffers from accurate calibration for water and is inaccurate while a proper detector is lacking. With KF-titration, very low water content can be determined (0.05 wt% in ethanol) while only one-two drops of condensate are required. During distillation, the feed composition changes since the component with the lowest boiling point is evaporated preferentially (until the azeotrope composition has been reached). In order to compensate for this change in feed composition, the residence time in the setup is calculated.

It is essential that heating up of the feed volume itself must be prevented since this would create a vapor phase with the normal composition as described by the VLE as shown in Figure 1. The infrared part of normal light will heat up the bulk liquid too fast and has to be prevented. For this, a flat plate filter was used between light source and feed volume, taking away the infrared part, when a normal white light lamp was used or sunlight.

Types of particles:

The principle behind heating up of the nanoparticles by light is the so-called plasmon resonance where electrons start combined resonance on the wave length of the light used which results in very fast heating of the particle. For this, very thin gold layers in the order of micrometers thickness need to be used. The thickness of the gold determines the optimum absorption wavelength of the used light which is shown in Figure 6:

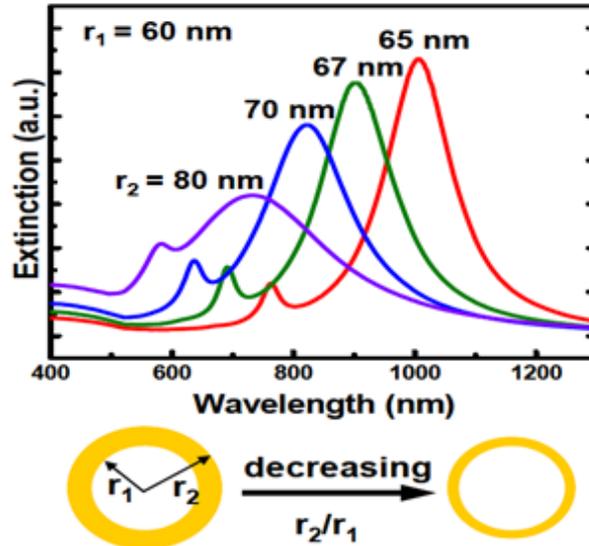


Figure 6: adsorption of light versus gold shell thickness

Also the part of the light which is adsorbed or scattered is depending on the particle size. The larger the particles, the higher the scattering. This is the reason for using nano-sized particles.

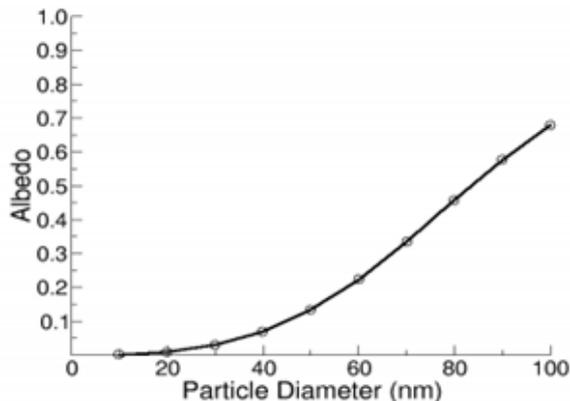


Figure 7: ratio of scattering and adsorption (Albedo) as function of the particle diameter

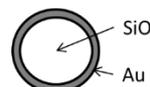
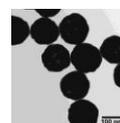
This results in two types of particles that could be used: nm pure gold particles and so-called nano-shells (as used in the article) where a core of e.g. silica is coated with a gold layer with a specific thickness. Conform the article, nano-shell particles have been obtained with a gold thickness of 20 nm and pure gold particles of 20 nm average diameter.

The nano-shell particles are extremely expensive so as alternative cheaper 20 nm pure gold particles were also purchased for initial tests. Both type of particles are supplied in water. In order to be able to make feed compositions of water/ethanol or water/propanol with a composition range as broad as possible and to be able to measure the entire composition range, the highest particle concentration is needed as can be bought. Evaporation of water prior to use could be considered but is not recommended because of agglomeration of the particles. Commercial pure gold particles and in particular the nano-shells can only be prepared in diluted systems. Without evaporation of water prior to use, this gives restrictions in the composition range.

The particle specifications are given below:

1. Particles from Nanocomposix: 20 nm Au-shell on SiO₂ (120 nm) spheres

- surface stabilizers present (PVP or PEG few nm layer)
- concentration 1.0 mg/ml = 5.4E+10 particles/ml, limited composition range possible without evaporation prior to use
- expensive (2300€ per 10 ml)
- $\lambda_{max} \sim 750$ nm



2. Pure Au-particles of 20 nm (size = Au-thickness nano-shell)

- 7.2E+11 particles/mL, almost full composition range possible
- λ_{max} 518-522 nm



3

Theoretical considerations

3.1 Light source

In order to know if a lamp can heat up the 20 ml bulk feed during distillation, which is undesirable, the power input of the available lamps were either calculated or experimentally determined:

- flat-plate led-based 630 nm lamp;

The lamp has a maximum output of 70 mW/cm² and is variable presuming that have of the feed bulb is lighted and presuming no heat loss to the environment. The following heats for evaporation have been used: 4.87E-2 MJ for pure water and 1.47E-2 MJ for pure ethanol. The time to evaporate 20 ml was calculated (at maximum power output) 3.71 hours for water and 0.78 for ethanol. The temperature increase, however, of the 20 ml feed was calculated 2.89°C/min for pure water and 5.10°C/min for pure ethanol which is too high for the distillation experiment. The lamp therefore has to be used at much lower output power.

- Normal 100 W (electrical) white light lamp;

A 100 W lamp and a Fresnel lens collimated the light was used with the 50 ml feed bulb. The lamp also irradiated infra-red light that is absorbed by the fluid and the container. This “background” heating was measured for pure water and for pure ethanol. For water 52 grams was heated. The temperature rose with 0.005 Kelvin per second. For ethanol, 40.8 grams were heated, which is about the same volume, resulting in a temperature increase of 0.007 K/s. Given the specific heat capacity of water of 4.184 J/gK and that of ethanol to be 2.43 J/gK, the heating power of the lamp for the IR light was calculated to be 1,1 to 0,75 Watt. This heating rate of the feed by the lamp is also too high for a normal distillation experiment.

As the temperature rose, the effect of a non-isolated system, resulting in heat loss to the environment, became more noticeable. The use of a filter between the fluid and the

Fresnel lens removed the infrared compound and the fluids remained at the same temperature. Filtering of the IR part should not influence the particle heating since the particles themselves do not adsorb this wavelength area.

The effect of the infrared shield is clearly visible in the following figure:

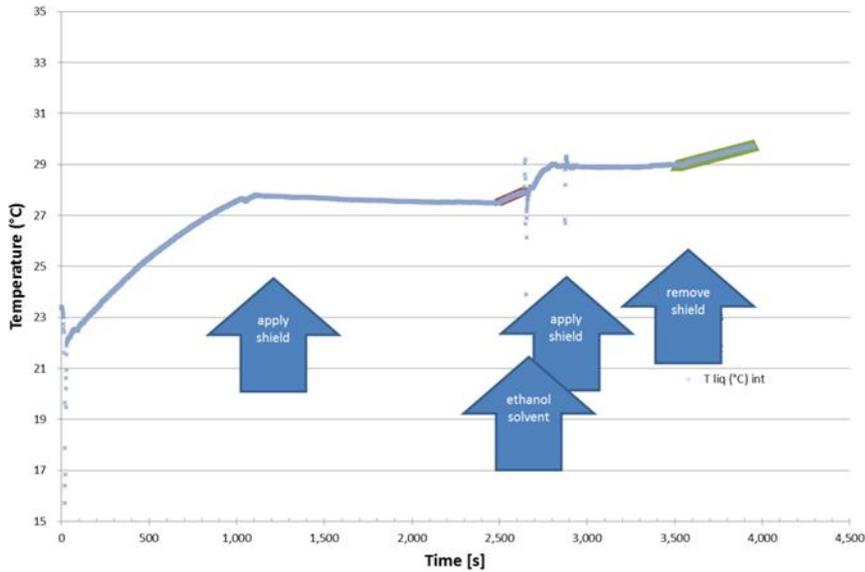


Figure 8: Effect of an IR heating shield when using a normal 100 W white light lamp

- Normal sunlight

The standard output used by the unit SE is a sun power output of 1000 W/m². Sunlight is not considered within the project.

3.2 Bubble stability in liquid media: Leidenfrost regime

When nanoparticles are superheated, the liquid adsorbed on the nano-particle surface rapidly evaporates, creating a nano-sized vapor layer that must form a nano-sized bubble that can escape from the bulk liquid without collapsing or (partially) condense (rectification). The bubble can only survive and escape the bulk liquid if the thermal conductivity of the vapor is low and inhibits heat transfer to the bulk. The vapor layer formed on the superheated surface can collapse below a critical particle surface temperature and will not be able to form a nano-sized bubble. If the bulk liquid is too

cold and the nanoparticles cool too much compared to the heating by the light source, nano-sized bubbles do not form (Leidenfrost regime).

Secondly, rectification may occur when formed vapor bubbles travel through the liquid attempting to escape from it (internal reflux). If the bulk liquid, however, is too high, escaped vapor bubbles mix up with normal evaporated bulk liquid and minimize the effect of non-equilibrium vapor composition as formed on the superheated surface of the nano-particles. This means that there is a very difficult to control balance between bulk liquid and actual temperature of the nano-particles. The last parameter depends on the power output of the lamp, the amount of light actually left at arrival to the particle surface which is dependent on the transmission of the light through the vessel (glass wall) and the travel distance from vessel wall to the particle surface.

3.3 Unknown distillation parameters

Since no hard data has been presented in the article and communication with the author did not result in hard facts, this hampered mimicking the reported experiment severely. Parameters like actual sun output power and distance of the Fresnel lens to the used glass vessel, are not known. Additionally, the bulk temperature at the moments of collecting condensate during the distillation experiments have also not been reported. This mere fact implies that actual results may highly depend on the actual shape and dimensions of the vessel used in conjunction with the light source specifications and e.g. travel distance of the light through the actual vessel. Up-scaling, if a positive effect is measured for light-induced breaking of azeotropes or at least deviations from the normal VLE, will be difficult if the relative contributions of each parameter mentioned is unclear. Much more research is needed then.

A parameter that might also play an (important) role, but independent of upscaling issues, is selective adsorption of water and ethanol on the particle surface, creating a non-equilibrium vapor phase when heated by the particle that is heated by the light. If adsorption differences (if any) contribute to the non-VLE situation in the vapor, is totally unclear.

In order to have at least some idea on power input into our experiments, the transmission properties of the used glass (Duran) was needed. From the manufacturer, a transmission of 90% over the entire relevant wave length area was obtained. So, only 10% loss of light power, adsorbed by the vessel glass wall, is expected.

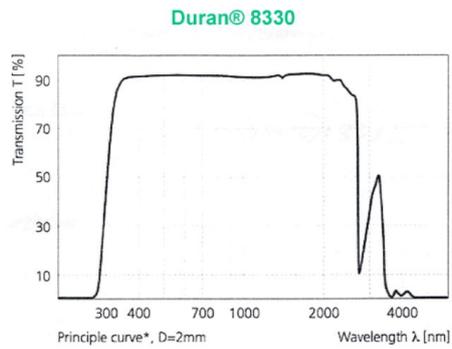


Figure 9: light adsorption through Duran glass

The 1000W white-light lamp has a spectrum comparable to normal sunlight, the actual power output at 40 cm distance from the lamp is ~ 1.3 kW. The used Fresnel lens has a surface area of 292 x 292 mm, comparable to the used Fresnel lens in the article (266.7 x 266.7 mm).

4

Results

4.1 Determination of bulk heating rate

A 100 W lamp was used in combination with a Fresnel lens with similar size as reported in the article and a round flask of 50 ml. The 630 nm lamp was disregarded since the wavelength is insufficient close to the adsorption maximum of the particles. The temperature increase of the fluid was measured with a thermocouple type K and recorded with a data logging system. The lamp also irradiated infra-red light that is absorbed by the fluid and the container. This “background” heating was measured for pure water and for pure ethanol. For water 52 grams was heated. The temperature rose with 0.005 Kelvin per second. For ethanol (absolute grade), 40.8 grams was heated, which is about the same volume, resulting in a temperature increase of 0.007 K/s. Given the specific heat capacity of water of 4.184 J/gK and that of ethanol to be 2.43 J/gK, the heating power of the lamp for the IR part of the light was calculated to be 1,1 to 0,75 Watt. Since the system is non-isolated, the increase in temperature of the liquid stops at a certain point (equilibrium).

The use of a filter between the fluid and the Fresnel lens removes the infrared compound and the fluids remains at constant temperature (see figure 6).

Repeating the experiment for a 50/50 water/ethanol mixture (20 ml) and 20 nm gold particles present (particle concentration conform the article = 2.5×10^{10} part/ml) resulted in a heating of the bulk of 7K until equilibrium of the bulk temperature occurred (from 25 to 32°C). This is unexpected since the bulk should (according to the article) heat up if the particles are active under light. This has also been observed by Neumann.

Two reasons could be the cause: the 20 nm particles are inactive under light and only real nano-shells possess this property (which according to theory is unexpected) or the lamp output power is too low in conjunction with the distance that the light has to travel through the bulb to have sufficient interaction with the particles.

To check on the lamp power output and the combination with the Fresnel lens (without the IR filter), the lamp was replaced by direct sunlight by execution of the experiment outside a building. This resulted for plane water (20 ml) in an initial heating rate of 35K/hr. With the 20 nm particles present, the initial heating rate (heating rate within the first few minutes) was 161 K/Hr. In 50 minutes, equilibrium is reached when the particles are present at a temperature of 58°C. Despite of the temperature increase of the bulk liquid, however, no water vapor could be seen or collected as condensate.

This experiment clearly showed the lamp to have insufficient power output compared to direct sunlight and a Fresnel lens. Therefore, another lamp was placed in follow up experiments with a much higher power output (1000 W electrical).

4.2 Distillation with nano particles

Since the 100 W lamp proved too low in output power, the 1000 W lamp was used in conjunction with a new vessel with less travel distance of the light through the bulk liquid. The vessel was double walled with on the inside a glass channel for water cooling. The nano-shells were used in this experiment.

A little amount of liquid could be collected in the condenser, 0.18 gram. From KF titration the water content was determined as 15.63 and 15.94 wt% (double check on the water content). The refractory index was found to be in relative accordance with these numbers (13,7 wt%).

From the normal VLE curve the condensate is enriched in ethanol (green point in Figure 10):

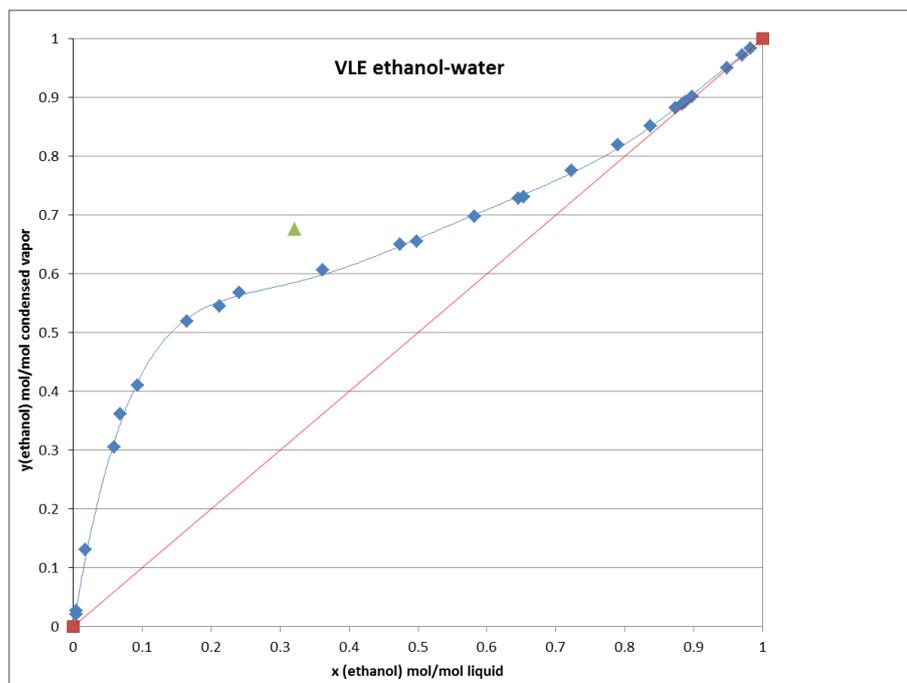


Figure 10: VLE curve of Ethanol water mixture in mol%. The green marker shows the composition of the distillate

The gold nanoshell (in 10 ml water) and 15 ml of ethanol mixture boiled at 82.5 °C which is consistent with the feed composition. The boiling was not continued by the irradiation of the lamp alone. When the heating fluid was cooled down from the 78 °C the boiling stopped. The 4 degree difference between heating fluid and nanoshell reactor fluid does not support a “Leidenfrost” boiling effect.

Since the experiment was run with water cooling on the inside of the glass vessel for ensuring that the bulk liquid does not heat up to normal boiling, the chance exists that the vapours created condense on the cooled glass wall and by further heating by the lamp, form a new vapour. This would mean that in the experiment, a normal distillation is carried out and the glass wall serves as a wall for subsequent distillation, so called rectification (presented in figure 8). If this is occurring, the prove of nano-particles responsible for shifting the composition of the vapour from the normal VLE curve, cannot be made.

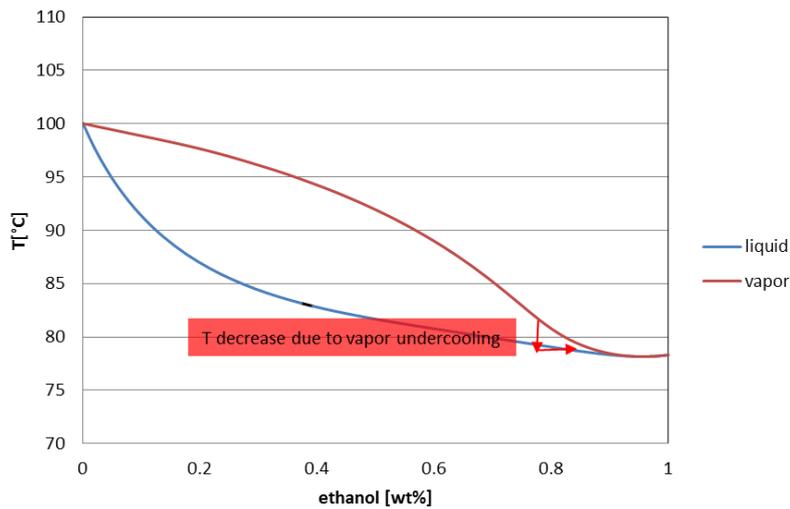


Figure 11: Rectification due to undercooling of vapour phase

In order to check if rectification is occurring, the experiment was repeated but without the internal water cooling and additional heating of the vapour by a heat gun. From KF titration the water content of the condensate was 21.12 wt%. From the VLE curve, the condensate composition is not deviating from the normal VLE curve (as shown by the purple point in Figure 10), showing that the effect in vapour composition is just an apparent shift and therefore a normal distillation tray:

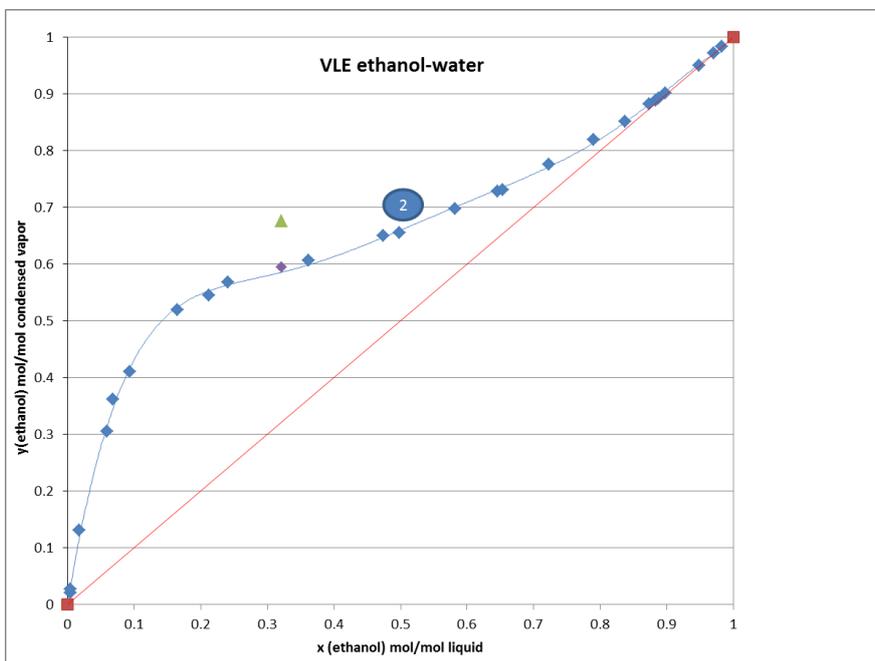


Figure 12: VLE curve of Ethanol water mixture in mol%. The purple marker shows the composition of the distillate

The effect of the shift is graphically shown in Figure 13.

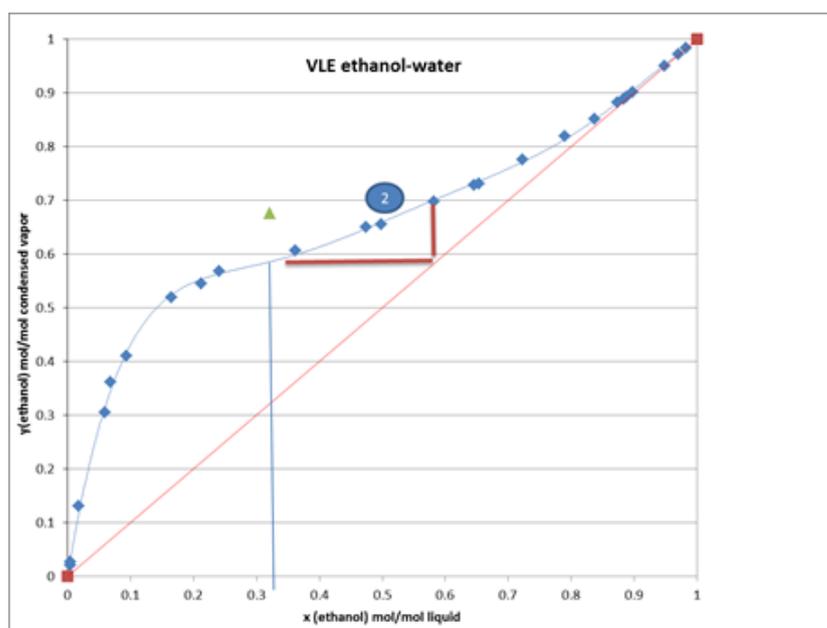


Figure 13: Principle of distillation trays

This experiment clearly shows that normal rectification is ongoing and that the presence of nano-particles and light has not changed the condensed vapour composition.

This effect might very well also be ongoing in the reported experiment of Neumann. Since no data in the reported experiments is known on actual bulk liquid temperatures at the moment of collecting condensate, this can however not be verified.

Additionally can be stated that in order to collect any condensate, the bulk liquid temperature already has to be quite close to the normal boiling temperature of the water/ethanol mixture composition. This would automatically decrease any effect on vapour composition by the presence of the nano-particles.

It is very unlikely that the reported experiments can be mimicked sufficiently since many parameters like actual light input, vessel glass wall thicknesses and bulk liquid temperature at the moment of collecting condensate are not known. If these parameters are very sensitive, presuming that the reported effect of the particles exists, this will automatically hamper any upscaling to realistic distillation volumes and possible designs of a distillation column.

It was noticed during the experiments that the nano-shells start to agglomerate. In communications with Neumann it was found that in her experiments, although not mentioned in the article, also agglomeration was observed. This agglomeration also hampers the experiments and has a negative effect on design of an actual distillation column for large scale application since this would mean that particles have to be fixed at a certain place. e.g. a wall inside the column.

In Figure 14, this agglomeration is shown:

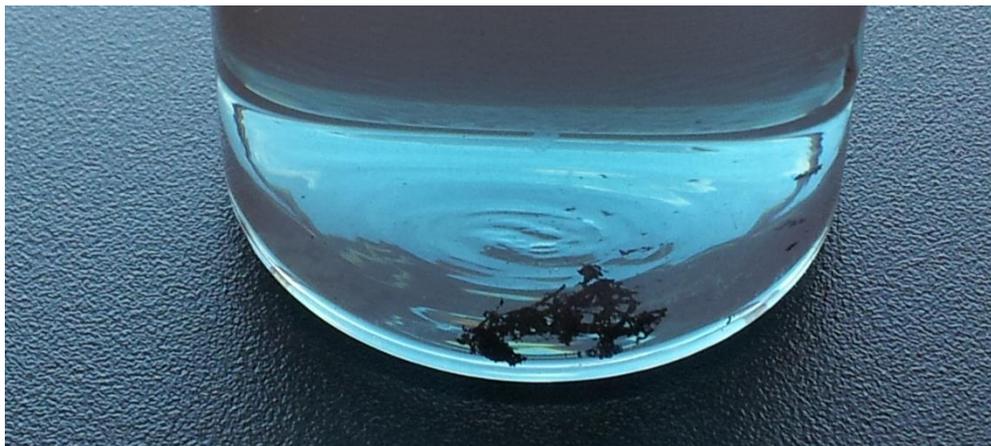


Figure 14: Agglomerated particles rinsed from the reactor

4.3 Distillation at direct sunlight

In the reported article, the experiment was conducted with normal sun light and a Fresnel lens. Despite of the fact that the project description clearly states that sun light is not included and light from lamps will be used, the lack of any real shift in vapour composition by heating the particles with lamps called for an experiment using direct sun light since in power output such an experiment would more closely mimic the reported experiment.. In Figure 15, the experiment under direct sun light is shown.

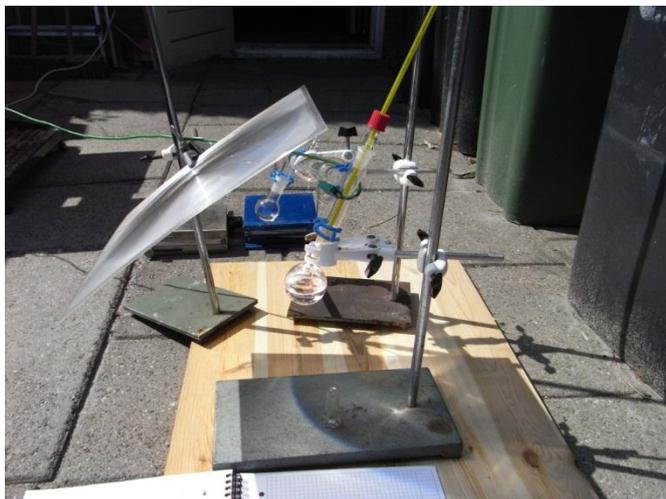


Figure 15: Set-up of the illumination test measuring the heating rate with nanoparticles

In the experiment, also a Fresnel lens was used for focussing the sunlight on the particles (the same size as the Fresnel lens in the article). The solution of the 20 nm

particles used here was $7.2 \cdot 10^{11}$ particles/ml (as-received). This was diluted with water and ethanol to a 50:50 wt% mixture with $2.5 \cdot 10^{10}$ particles/ml, conform the particle concentration in the reported experiment.

Heating rates (without any filter) for plain water amounted to 35 K per hour. Initial heating rate of the nanoparticle dispersion was determined to be 161 K per hour so the particles accelerated the bulk heating. This was, however, only achieved for a small period. After some time the heat losses to the ambient were giving an almost constant temperature.

During the actual distillation the bulk temperature rose to 58 °C and remained stable at this temperature. There were, however, no signs at all of vapour transport in the distillation column, the condensor or collecting vessel.

The focal point was checked with a piece of paper that caught fire almost immediately so the Fresnel lens worked properly.

With the use of direct sun light, no condensate could be collected and therefore a check on possible vapour composition shifts was impossible. Earlier experiments with the lamp already showed that a much higher bulk temperature was needed (see section 4.2) before any small amount of condensate could be collected. This higher bulk temperature is already so close to the normal boiling point of the water/ethanol mixture that it can only be expected that a normal VLE composition will be measured when sufficient condensate could be collected.

The experiment under direct sun light therefore did not result in a better understanding. It should be remarked that in the reported experiment in literature, a true lux measurement of the actual power input of sun light, condensed by the Fresnel lens, into the bulk is lacking which compromises actual mimicking the experiments.

4.4 Preliminary economics

Although in the project it was shown that the reported results of breaking of azeotropes with sun and gold particles could not be reproduced, preliminary economic calculations to evaluate the capital costs of a large scale installation was performed. In the calculations it was assumed that an additional distillation column for breaking azeotropes will be used in which the gold particles will be coated on a foam structure so as to prevent any unwanted agglomeration. Removal of remaining water from ethanol above the azeotropic point by the use of molecular sieves was considered as a conventional process (Technical Report NREL). The assumed ethanol production capacity is 2000 metric t/day. Since in this case a column with coated golden particles will replace the molecular sieves, the height of the coated foam to have a comparable capital costs to the sieves was calculated. Input data are given in the following table:

Table 1: Molecular sieves compared to gold particles

Parameter	Value
Molecular sieve installed costs (\$), ref. year 2007, material stainless steel (NREL)	3,112,319
Correction factor stainless steel plates 2012/2007 (DACE)	111
Diameter distillation column (m) (NREL)	3.5
Gold price, \$/kg, average 2010-2012 https://www.bullionvault.com/gold-price-chart.do	45,988
Coating density [kg/m ³]	10
Foam specific surface area [m ² /m ³] (Boomsma, 2002)	820
HETP, m (Sulzer)	0.3

In the calculations the following assumptions have been applied:

- same flooding regime for trays and foam, same diameter of azeotrope column as for a tray distillation column;
- cost of the gold will govern the capital costs of azeotrope column, thus only cost of the gold will be used in the calculations. Note: the costs of gold solution will be higher than the gold costs since the preparation of gold coated nanoshells is costly;
- equilibrium stage height in the foam is the same as for a structured packing.

Assuming this, it can be calculated that 1 m of foam can be coated with gold for the same costs as molecular sieves. This will mean approximately 3 equilibrium stages. Since, this column is used for breaking of the azeotrope where the equilibrium line is close to the x=y line, this amount of stages may not be enough. Installing more stages will lead to highly increased capital costs of 1,327,369 \$/ additional stage.

It is recognized that these calculations are rather simple. However, they show that, compared to removal of remaining water in ethanol/water distillation, the rough estimate of a gold-nanoparticle type of distillation would be economically unfavorable.

It has to be noted that re-use of the gold metal is not included in these calculations. The costs of regaining the metal when required and conditioning of the metal for re-use is unknown. However, the actual price of the gold nanoshells is much higher than the pure gold price that has been used in the calculations.

It should also be noted that the nanoshells cannot be prepared in one large batch production (information from the company), nor in higher concentrations. Upscaling of the nanoshells to suitable quantities aiming on lower production costs is, therefore, questionable.

5

Conclusions

The breaking of the ethanol/water azeotrope by light-heated gold-coated nanoparticles, as reported in literature, could not be confirmed by us, despite of many attempts. Several parameters have been identified during our experiments that actually hamper exact mimicking of the reported experiment that has led to the conclusion that in this way, such azeotropes can be broken. It should be realized that, next to the very poor mimicking of the reported experiment, the errors in the particular experiment are very large and that the conclusion of breaking the mentioned azeotrope should not have been made in the first place. For such a statement, a more thorough investigation with more exact data should be made first. In our view it can, however, not be totally excluded that the phenomenon exists.

Even when the reported phenomenon would exist, economics of using gold-coated particles are very unfavourable compared to the use of e.g. zeolites as water absorbers, based upon a rough estimate of material use and costs. It is therefore not recommended to further pursue this work.

6

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ECN

Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949

F +31 88 515 8338

info@ecn.nl

www.ecn.nl