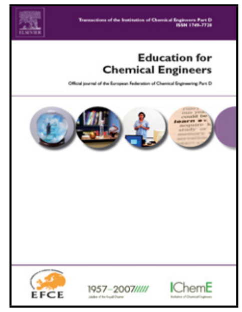
## Accepted Manuscript

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# Graphic web–apps for teaching ternary diagrams and liquid–liquid extraction

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Highlights

- Web–apps for teaching of liquid–liquid equilibria and extraction were developed
- The apps have a strong free-hand feel for visual and kinaesthetic engagement
- Students' marks improved; gap between poorer and better performing students reduced
- Students felt the apps increased their understanding of liquid–liquid extraction

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**Abstract:** Recent years have seen a rapid development in e-learning technologies. Specific topics; however, may require additional teaching tools created particularly for their unique characteristics. It is important that these tools are developed with learning outcomes in mind, and if possible are in a format easily accessible. We have developed graphic web applications for the teaching of liquid–liquid equilibria, single– and multi–stage liquid–liquid extraction using ternary phase diagrams. These applications allow students to draw liquid–liquid 2-phase equilibrium curves, calculate phase separation for a given mixture and graphically determine equilibrium stages; the correct results are then produced with hints for the students if they get stuck. Student usage figures and opinions have been collected for the application during trial use on a combined full-time taught and distance learning course in Engineering Separations at The University of Manchester. The current students have found these applications useful for developing their understanding of liquid–liquid equilibria.

*Keywords; web–app, ternary diagrams, interactive tutorials, plotting graphs.*

## 1. INTRODUCTION

E-learning technologies provide educators an ever growing array of tools, many of which are integrated in Course Management Systems (CMS) or Virtual Learning Environments (VLE). Along with modern multimedia and chat support services, these systems have user-friendly facilities for creating on-line assignments from a variety of pre-set question types. Amongst others, these types typically include "Fill in the Blank", "Multiple Choice", "Calculated Numeric", and "Hot Spot" formats, the last being useful when students need to identify and pinpoint a specific location in a diagram or image. Despite the large number of choices and in-built flexibilities, certain subjects require uniquely structured question types not available in CMSs.

Simulation-based educations tools aim to offer a rich and dynamic learning experience by allowing the user to interact with a model of a physical system via adjusting parameters and watching the corresponding response. Mathematica-based Wolfram Demonstrations Project (Wolfram Research, Inc., 2017) and R-based Shiny (RStudio, Inc., 2017) packages have been widely used to produce high quality teaching materials. Yet demonstrations designed with these software do not facilitate enhanced engagement enabling users to attempt questions through visual/kinaesthetic interactions with the graphic interface.

Liquid–liquid equilibria calculations are an essential part of a chemical engineer's education. For a ternary system, suitable for liquid–liquid extraction (LLE), these calculations involve plotting and using data in an equilateral triangle graph. Describing three-component systems this way, using ternary diagrams or tri-plots, often in the context of phase domains is a popular method in science and engineering. Ensuring that students understand and are readily able to use such a broadly applicable tool is, therefore, very important.

Students first learning about ternary diagrams often find the concept of mapping the possible states of a three-component system onto a triangular domain challenging. Thus, mastering the ternary plot requires a lot of practice. Current applications available for liquid–liquid equilibria and liquid–liquid extraction lack the ability for students to practice problems, they simply allow students to manipulate variables to only see changes, not calculate these changes themselves (Baumann, 2015; Binous *et al*., 2015; Binous, 2006).

Falconer and Nicodemus (2014) create and implement a large number of Mathematica Simulations, within courses at the University of Colorado Boulder, which allow students the ability to change input parameters and examine how this affects output graphs. Several of these simulations are based around separation techniques. These simulations are also linked to multiple choice questions to test student learning. Student feedback was generally positive, with students indicating that it enhanced their understanding beyond the use of the textbook with a score of 6.8/10 (with 5/10 being no difference).

Granjo *et al*. (2012) discuss the creation of a virtual platform called LABVIRTUAL by the Universities of Coimbra and Porto, which includes material on separations. The platform includes texts, figures, and animations aiming to get the student acquainted with the subject followed by simulations which can be used for investigating the effect of changing parameters on the equipment design or to provide results in a virtual experiment which can then be compared to literature results. Student feedback reported within the paper was generally positive, with all students finding some level of usefulness for separations.

Teppaitoon (2016) directly focuses on liquid–liquid extraction and provides students with an excel spreadsheet method for solving multi-stage liquid–liquid extraction examples. The stage-by-stage calculation procedure is carried out in excel with the option to plot the results on a ternary diagram if needed. Unfortunately, no formal quantitative student evaluation was conducted for this implementation; however, the author noted that the students paid more attention to the subject.

The simulation-based teaching tools discussed above lack the ability for students to fully carry out the procedure themselves (Teppaitoon (2016) does convert the procedure into an Excel based procedure) as would be achieved with pen and paper. The web–apps introduced here were designed to have a strong free-hand feel allowing students to retain the enhanced visual and kinaesthetic engagement with the material, while giving students the opportunity of practicing on a large number of randomly-generated exercises. The apps also give students the option of skipping to the sections they wish to practice, e.g. if they want to practice calculation of the separation they can get a generated equilibrium curve instead of having to plot this first.

Moreover, incorporating graphic student input along with numeric answers into demonstration-based tools is important for student learning as this allows them to practice and apply knowledge they have learnt. The software was developed to be complementary to the teaching and to ensure that students can confidently carry out liquid–liquid equilibria, single– and multi–stage liquid–liquid extraction calculations.

## 2. SOFTWARE

The latest version of the HyperText Markup Language (HTML5) provides enhanced functionality through comprehensive application programming interfaces (APIs) for graphic content alleviating the need for plug-ins like Adobe Flash, ActiveX or Java applets. Today's web applications relying solely on HTML5, JavaScript (JS) and Cascading Style Sheets (CSS) offer a fast, dynamic, visually rich, and highly interactive experience. These slim single-page applications (SPA) are becoming ever more popular thanks to the rapid spread of low-powered devices such as smartphones and tablet computers. Our SPAs were made available as an optional practice tool for students attending the Advanced Engineering Separations module via the Virtual Learning Environment (Blackboard) of The University of Manchester. The apps do not download pre-formatted images and/or tables into the page. Instead, all necessary information is stored in ASCII text files (one for each three-component system) on the web server and every visual element is generated at the front end. This makes setting up the exercises quick and easy only requiring a text editor.

The apps divide the screen into three panels: (I) a column on the left separated from the rest of the screen by a vertical line; (II) a rectangular area above the triangle; and (III) a standard, fully-labelled ternary triangle with buttons underneath (screenshot shown in Figure 1). (I) is for displaying miscibility and mutual equilibrium data tables, also used for collecting numeric answers and outputting corresponding numeric solutions. Questions and hints are shown in (II), whereas (III) serves as graphic core for free-hand interaction. To familiarise students with the two frequently-used ways of labelling tri-plots, component names are placed either at the vertices or parallel to the sides. In addition, the columns of the Equilibrium Miscibility Data table are randomly assigned to the components. The left and bottom axes are also flipped irregularly between exercises. In all apps, students are given the option of aborting the exercise at any stage by clicking "Hit Me" which takes them back to a refreshed first screen. The apps neither recorded nor marked answers.

*2.1 Drawing Ternary Phase Diagrams*

Made available in the 2015–2016 academic year, the task for students is to add points (black circles) using the compositions provided in the upper table to outline the curve between the region of homogeneous mixtures and the domain characterised by phase separation. They can switch to “Erase” mode to remove any unwanted points from the diagram before going back to “Draw” mode to continue. When they are satisfied with the location of the points they click “Next” to reveal the solution. The app only allows them to proceed if they added as many points as the number of rows in the Equilibrium Miscibility Data Table. Pressing “Next” again takes them to the tie line drawing module which retains the correct 2-phase boundary from Question 1 as guidance. Using the “Draw” or “Erase” modes, students in Question 2 now required to populate the diagram with tie lines by placing black squares to where the end points are located. If the number of lines is right, the app unlocks the “Next” button and students can continue onto the solution (Figure 2b), followed by pressing “Done” to load a new exercise.

*2.2 Single–stage LLE*

This app, also introduced in 2015–2016, focuses on the total composition of a mixture when a Feed (F) is put into contact with Solvent (S) where the composition of the former and the S/F mass ratio are randomly assigned. The “Draw” and “Erase” buttons are replaced here with “F”, “S” and “M” buttons. Students can place these entities on the diagram individually by pressing the corresponding button first, followed by clicking at the desired location. The chosen positions are only temporarily locked at this stage, students are allowed to move F, S and M around freely until the composition of the mixture (M) is entered on Panel I and “Next” is pressed. The hint for this exercise is a line drawn between S and F without identifying the end points (Figure 3a). To make it easier for students wishing to place F, S and M without using the hint an auxiliary line drawing function is provided. Once all three points are added and the composition of M is entered, students reveal the solution (Figure 3b) by clicking “Next”.

In the second stage, loaded by pressing “Next” after the solution to Question 1 is examined, students are asked to position and input the compositions of the two phases the total mixture, M, separates into. Like before, the location of phases A and B produced in this step can be added to the diagram, and subsequently moved around, by clicking buttons “A” or “B” (Figure 3c). When the positions of the two phases are finalized and their compositions are entered, students press

"Next" to uncover the solution (shown in Figure 3d) and finally "Done" to finish and return to Question 1 with a new set of data and parameters.

*2.3 Multi–stage LLE*

This app, available from 2016–2017, is based on the Hunter–Nash method (Hunter and Nash, 1934) and exercises are comprised of four tasks. The opening task is similar to that of Single–stage LLE (Figure 4a,b), followed by a question regarding the extract composition ($E_1$) given the flow rates of the feed and solvent solutions as well as the composition of the raffinate ($R_N$). Students are asked to enter the numeric value of the weight percent of each constituent and to stick the $E_1$ and $R_N$ points on the diagram (Figure 4c). Once all required fields are filled and $E_1$ and $R_N$ added, students reveal the answers by clicking "Next" (Figure 4d). Pressing "Next" again takes them to the task of determining the location of the Operating Point, Δ, using Operating Lines with the aid of $E_1$, $R_N$, S and F carried over from the previous step (Figure 4e). After the Operating Lines are drawn and the Operating Point is placed on the canvas, once again, students move on to the solution of this part by pressing "Next" (Figure 4f). In the last block, students are asked to determine the number of equilibrium stages by constructing lines between relevant points in the diagram. Lines can be cleared, if necessary. Once the stages are stepped off and the numeric value of the number of equilibrium stages entered, the answer displays upon clicking "Next". Pressing "Done" brings students back to Q1 with refreshed parameters and components.

Students, depending on their confidence, can adopt three different strategies or a combination of them to complete the steps of these exercises. Some may choose to carefully consider the position of each point and make calculations before entering the compositions without using hints, while others may feel more comfortable using the extra bits of information offered. It is also possible to simply make up answers along the way and watch as the solution unfolds step by step. Thanks to the large number of combinations, students can even decide to start out by just coasting through the apps and then slowly become more and more engaged without encountering the exact same set of questions twice.

## 3. STUDENT USE

The web–apps were tested using the students taking a combined 3$^{rd}$ year undergraduate and MSc module at The University of Manchester (Advanced Engineering Separations) and were available to the students as a link in the module's page on Blackboard.

Figure 5 shows the aggregate number of uses of the web–apps over the period of the course. There are several key events in the course that trigger the use of the apps. The first period of use is during the time that the topic of liquid–liquid extraction was taught to the students; 6$^{th}$-30$^{th}$ October. The largest peak in this period is just before and during the first coursework which included the topic of liquid–liquid extraction and contained questions relating to the web–apps. The second period of use starts on the 21$^{st}$ November, this was unexpected as a topic unrelated to LLE was being taught (azeotropic distillation sequencing). However, this topic involved the use of ternary diagrams so the students were independently using the tool to remind themselves of the use of ternary diagrams.

The pattern of use of the web–apps is very similar, with more use of the plotting of the phase boundary system,

Ternary Phase Diagrams – 966
Single–stage LLE – 761
Multi–stage LLE – 684

The third period of use is during revision for the final exam (25th January), unsurprisingly this is where the majority of the use of the web–apps is. When asked, students commented that they liked the ability to practice the questions multiple times with different options, one student's comment was, "*It is indeed a very good way for student who would like to do more practices and consolidate their knowledge. I would strongly recommend these questions to other students!*".

Usage statistics did not allow for analysing student progression and hint request patterns, or monitoring the level of student engagement.

## 4. EVALUATION

To allow students to practice for a first coursework, a compulsory formative quiz was given to them. Five questions in this quiz were based on liquid–liquid extraction topics related to the web–apps. The marks for these questions increased from 77% to 91% with the introduction of the apps. Table 1 shows the results for the final exam that was given to the students during the last three years. Design of multi–stage liquid–liquid extract features on the exam as due the general use of ternary diagrams. The introduction of the *Multi–stage LLE* app for 2016–2017 has contributed to a rise in scaled student mark, showing greater student learning, and a reduction in the scaled standard deviation, showing that there is less of a gap between poorer and better performing students.

At the end of the course an evaluation questionnaire was answered by the students, this had a 40% return rate and the result for the question "The eLearning resources provided in this unit enhanced my learning experience" gained an average mark of 4.69/5.0, with the distribution given by Figure 6.

To analyse the web–apps in more detail the iTeach (iTeach, 2016) questionnaire (developed to assess the efficiency of individual pedagogical approaches; Glassy, 2016) was also given to the students which had about a 25% response rate for the class, this questionnaire asked many in depth questions about the whole course, but it also focused on the web–apps as well. Figure 7 shows the results of the survey from the questions most closely related to the web–apps; the average scores are given in Table 2.

It is clear that students did like the web–apps and felt they improved their understanding of liquid–liquid extraction. They also thought that the apps allowed them to evaluate their own learning progression as they attempted the questions. The top comment from the students was that they liked the fact they could get hints for the questions rather than just having the answered revealed.

Figure 8 presents the summary of the iTeach survey undertaken by the students, the closer to 5 in each category the higher the rating in that category. Categories 3 and 4 were the most relevant to the web–apps and can be seen to be scores above 4 out of 5. Category 5 is related to the increase in learning that the students have received based on the introduction of new course elements, and again is score is high at almost 4 out of 5.

## 5. CONCLUSIONS

A HTML5/JS/CSS-based, interactive, graphic web–apps were developed for the teaching and learning of LLE using ternary diagrams, and was trialled by chemical engineering students at The University of Manchester. The students liked using the web–apps and felt that it aided their understanding. The authors feel encouraged by the positive student feedback and the improved exam results showing that understanding was gained by the students. As one student wrote, "*These are well-designed online questions that helps students better understand how to do this type of questions. The step-by-step method, together with hints, is easy for students to follow and think.*". Development is currently underway to include azeotropic distillation sequences, and to design similar web–apps for other areas of (chemical) engineering and science.

## ACKNOWLEDGEMENT

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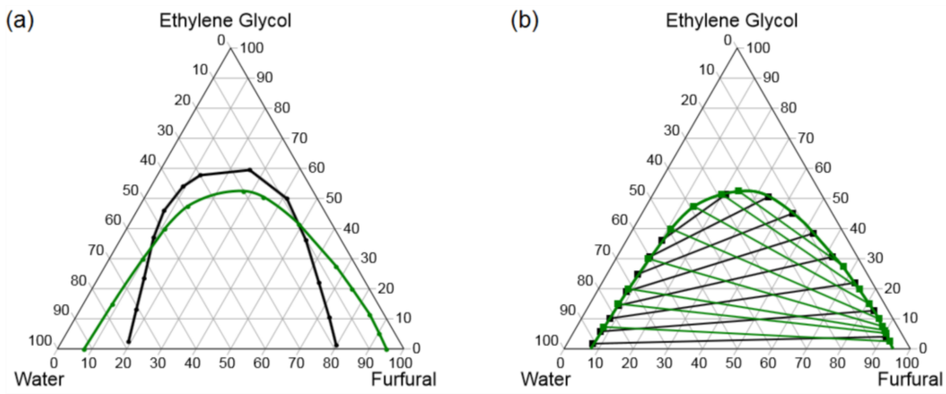



| Equilibrium miscibility data | | |
|---|---|---|
| Water | Ethylene Glycol | Furfural |
| 5.0 | 0.0 | 95.0 |
| 4.5 | 5.2 | 90.3 |
| 4.1 | 11.5 | 84.4 |
| 4.9 | 20.0 | 75.1 |
| 5.8 | 27.5 | 66.7 |
| 9.5 | 41.5 | 49.0 |
| 15.2 | 50.5 | 34.3 |
| 20.0 | 52.5 | 27.5 |
| 38.6 | 47.5 | 13.9 |
| 49.0 | 40.0 | 11.0 |
| 60.3 | 30.0 | 9.7 |
| 76.6 | 15.0 | 8.4 |
| 92.3 | 0.0 | 7.7 |

| Mutual equilibrium data | |
|---|---|
| Ethylene Glycol in Water | Ethylene Glycol in Furfural |
| 52.5 | 27.5 |
| 51.5 | 20.0 |
| 47.5 | 15.0 |
| 40.0 | 10.0 |
| 30.0 | 7.5 |
| 20.0 | 6.2 |
| 15.0 | 5.2 |
| 7.3 | 2.5 |

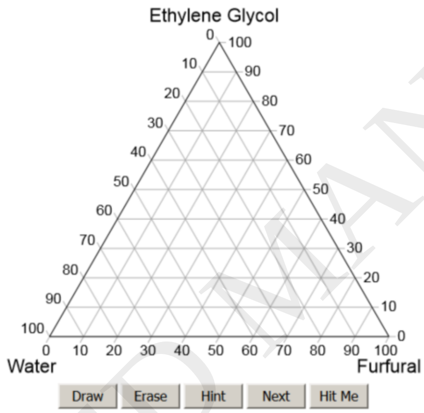
I

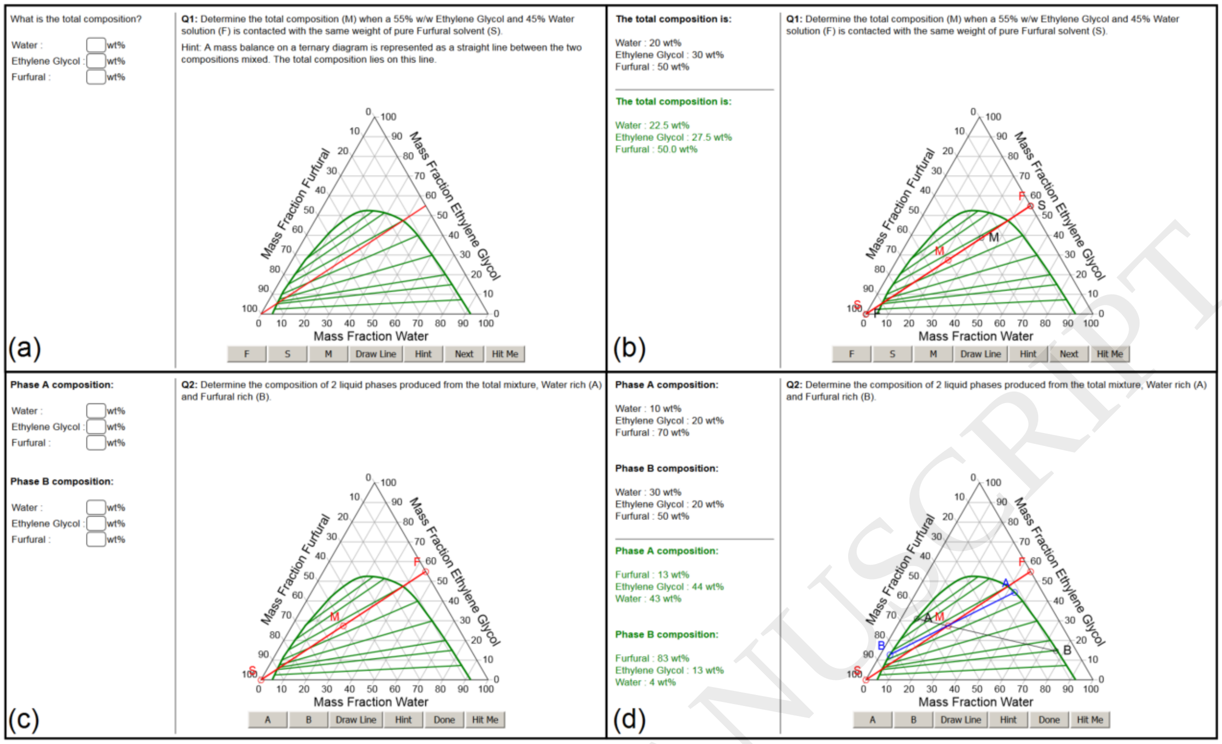
**Q1:** Use the data in the tables provided to draw the liquid-liquid 2-phase boundary on the ternary diagram below.

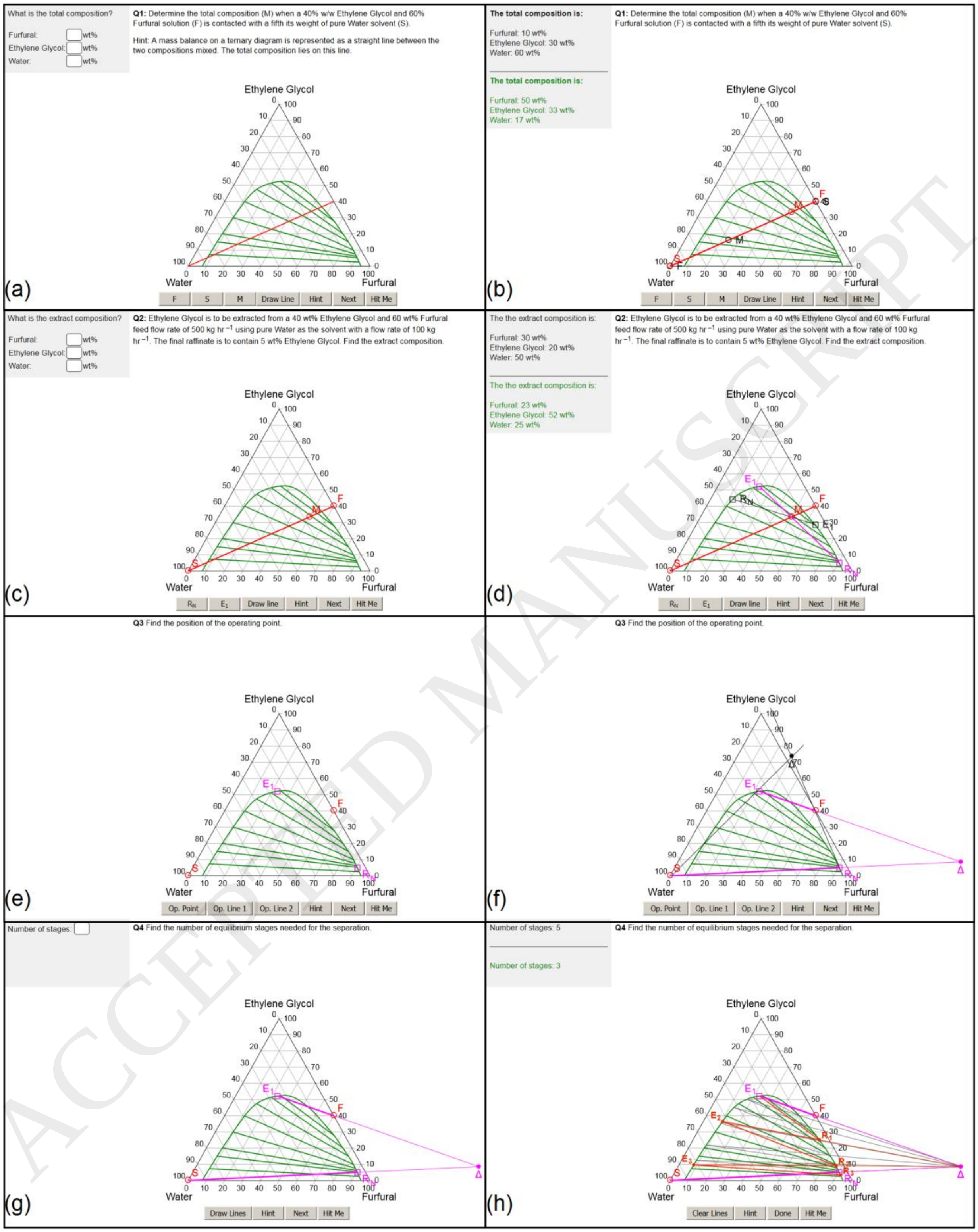
Hint: The 2-phase boundary is the boundary between the region where the 3 liquids form 2 separate phases at equilibrium.

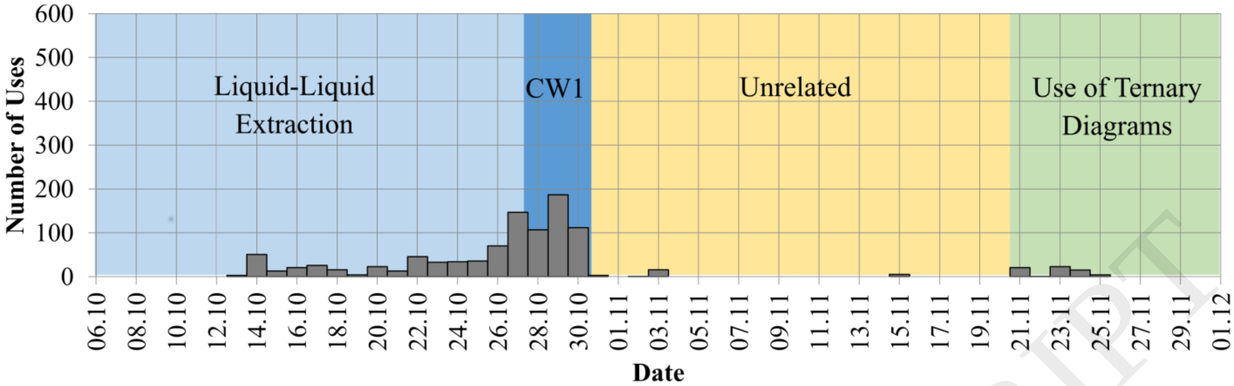
II

III

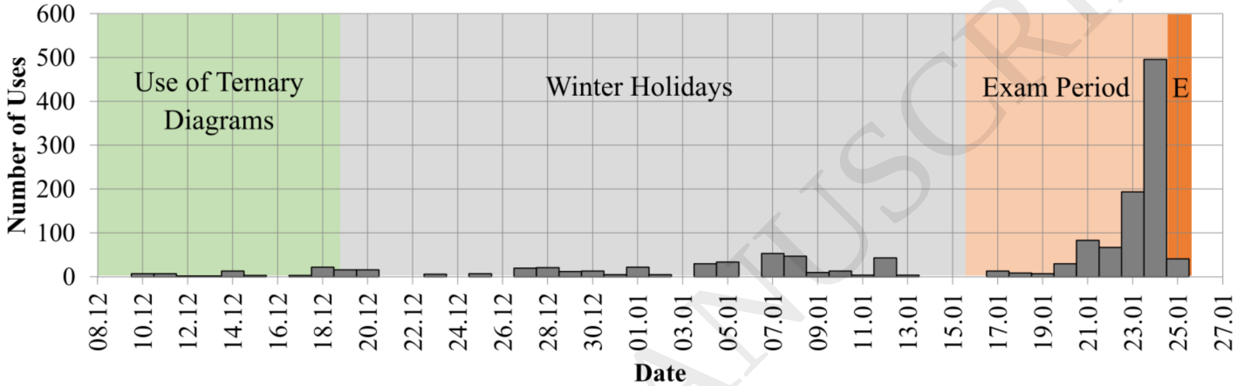



What is the total composition?
Water : wt%
Ethylene Glycol : wt%
Furfural : wt%
Q1: Determine the total composition (M) when a 55% w/w Ethylene Glycol and 45% Water solution (F) is contacted with the same weight of pure Furfural solvent (S).
Hint: A mass balance on a ternary diagram is represented as a straight line between the two compositions mixed. The total composition lies on this line.
Mass Fraction Furfural
Mass Fraction Ethylene Glycol
Mass Fraction Water
F S M Draw Line Hint Next Hit Me
(a)
The total composition is:
Water : 20 wt%
Ethylene Glycol : 30 wt%
Furfural : 50 wt%
The total composition is:
Water : 22.5 wt%
Ethylene Glycol : 27.5 wt%
Furfural : 50.0 wt%
(b)
Phase A composition:
Water : wt%
Ethylene Glycol : wt%
Furfural : wt%
Phase B composition:
Water : wt%
Ethylene Glycol : wt%
Furfural : wt%
Q2: Determine the composition of 2 liquid phases produced from the total mixture, Water rich (A) and Furfural rich (B).
A B Draw Line Hint Done Hit Me
(c)
Phase A composition:
Water : 10 wt%
Ethylene Glycol : 20 wt%
Furfural : 70 wt%
Phase B composition:
Water : 30 wt%
Ethylene Glycol : 20 wt%
Furfural : 50 wt%
Phase A composition:
Furfural : 13 wt%
Ethylene Glycol : 44 wt%
Water : 43 wt%
Phase B composition:
Furfural : 83 wt%
Ethylene Glycol : 13 wt%
Water : 4 wt%
(d)


What is the total composition?
Furfural: wt%
Ethylene Glycol: wt%
Water: wt%
Q1: Determine the total composition (M) when a 40% w/w Ethylene Glycol and 60% Furfural solution (F) is contacted with a fifth its weight of pure Water solvent (S).
Hint: A mass balance on a ternary diagram is represented as a straight line between the two compositions mixed. The total composition lies on this line.
Ethylene Glycol
Water
Furfural
(a)
F
S
M
Draw Line
Hint
Next
Hit Me
The total composition is:
Furfural: 10 wt%
Ethylene Glycol: 30 wt%
Water: 60 wt%
The total composition is:
Furfural: 50 wt%
Ethylene Glycol: 33 wt%
Water: 17 wt%
(b)
What is the extract composition?
Q2: Ethylene Glycol is to be extracted from a 40 wt% Ethylene Glycol and 60 wt% Furfural feed flow rate of 500 kg hr$^{-1}$ using pure Water as the solvent with a flow rate of 100 kg hr$^{-1}$. The final raffinate is to contain 5 wt% Ethylene Glycol. Find the extract composition.
(c)
The the extract composition is:
Furfural: 30 wt%
Ethylene Glycol: 20 wt%
Water: 50 wt%
The the extract composition is:
Furfural: 23 wt%
Ethylene Glycol: 52 wt%
Water: 25 wt%
(d)
Q3 Find the position of the operating point.
Op. Point
Op. Line 1
Op. Line 2
(e)
(f)
Number of stages:
Q4 Find the number of equilibrium stages needed for the separation.
Draw Lines
(g)
Number of stages: 5
Number of stages: 3
Clear Lines
Done
(h)



Number of Uses
600
500
400
300
200
100
0
Liquid-Liquid Extraction
CW1
Unrelated
Use of Ternary Diagrams
06.10
08.10
10.10
12.10
14.10
16.10
18.10
20.10
22.10
24.10
26.10
28.10
30.10
01.11
03.11
05.11
07.11
09.11
11.11
13.11
15.11
17.11
19.11
21.11
23.11
25.11
27.11
29.11
01.12
Date

Number of Uses
600
500
400
300
200
100
0
Use of Ternary Diagrams
Winter Holidays
Exam Period
E
08.12
10.12
12.12
14.12
16.12
18.12
20.12
22.12
24.12
26.12
28.12
30.12
01.01
03.01
05.01
07.01
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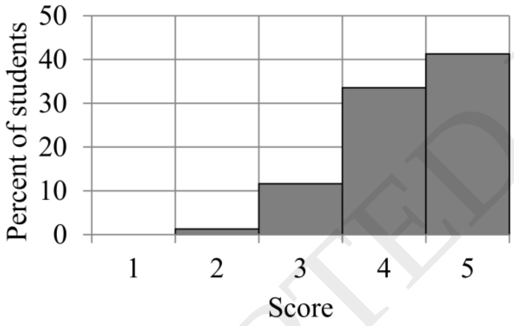
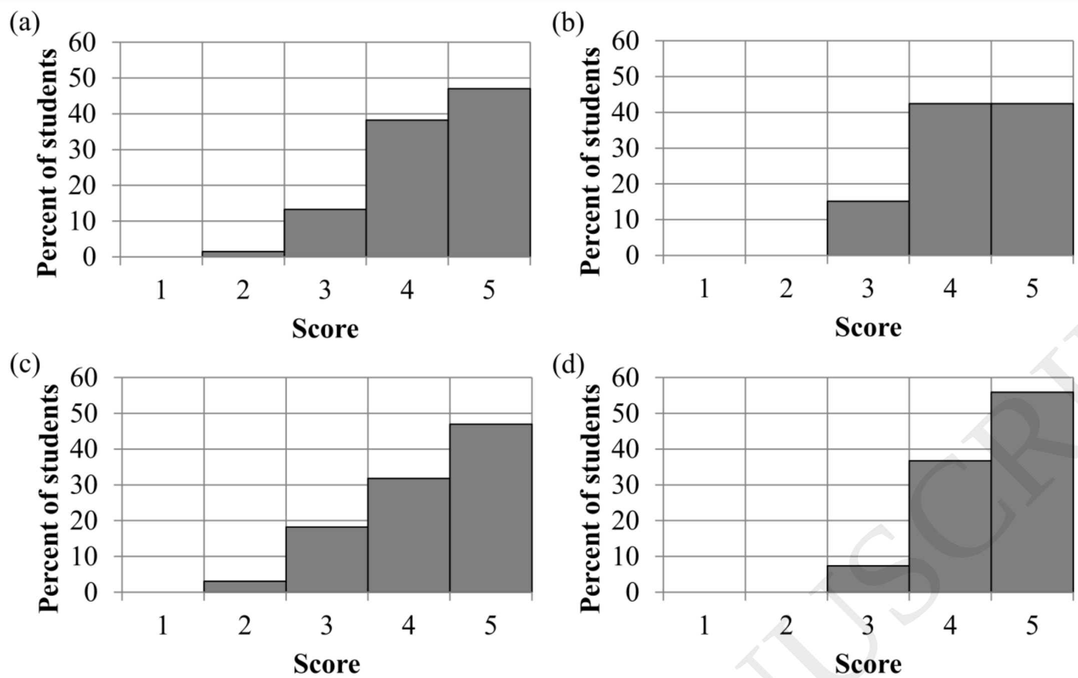
25.01
27.01
Date

Percent of students
50
40
30
20
10
0
1
2
3
4
5
Score



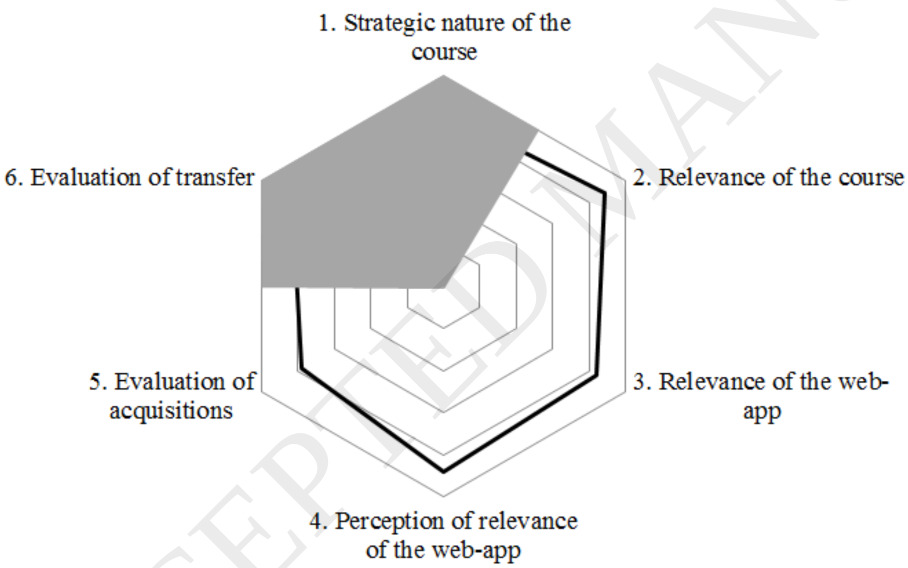




**Figure 1. Layout of ternary web–app with Hint for Question 1 revealed. The three panels are highlighted with dotted lines.**

**Figure 2. (a) 2–phase bonudary and (b) tie lines: student input (black) and app-generated solutions (green).**

**Figure 3. Phase separation in a single step operation.**

**Figure 4. Multi–stage liquid–liquid extraction.**

**Figure 5. Uses of the web–app during the course (October 2016 to January 2017), CW1 is the coursework related to liquid–liquid extraction, and E is the final exam.**

**Figure 6. Student responses to "The eLearning resources provided in this unit enhanced my learning experience" – 5 is Agree, 1 is Disagree.**

**Figure 7. Student responses to (a) Do the web–apps improve the teaching?, (b) Do the web–apps enable the evaluation of the learning progression?, (c) Did the web–app approach allow me to understand the subject better?, and (d) Was the quality of the web–apps appropriate? – 5 is "Absolutely / Strongly Agree". 1 is "Absolutely Not / Strongly Disagree" .**

**Figure 8. Results of iTeach survey based on the data collect from the students, categories 1 and 6 do not have student components, and thus have no rating. Scale runs from 0 at the centre to 5 on the outside.**

**Table 1. Average student mark over 5 questions on a compulsory formative quiz on plotting and using ternary diagrams for liquid–liquid extraction.**

| **Year** | **2014–2015** | **2015–2016** | **2016–2017** |
|---|---|---|---|
| Number of Students | 118 | 221 | 317 |
| Mark / 2$^{nd}$ year mark | 0.950 | 0.950 | 1.032 |
| Standard deviation / 2$^{nd}$ year standard deviation | 1.301 | 1.274 | 1.073 |

**Table 2. Summary of the student responses to questions about the web–app.**

| **Question** | **Average Score / 5.0** | **Standard Deviation** |
|---|---|---|
| Do the web–apps improve the teaching? | 4.31 | 0.75 |
| Do the web–apps enable the evaluation of the learning progression? | 4.27 | 0.71 |
| Did the web–apps allow me to understand the subject better? | 4.23 | 0.85 |
| Was the quality of the web–apps appropriate? | 4.49 | 0.63 |