環境グリーンプロセス
Green Chemical Processes

Richard Smith
東北大学 環境グリーンプロセス学　超臨界流体工学

Tohoku University
Department of Chemical Engineering
Graduate School of Environmental Studies
Sendai, Japan
http://www.che.tohoku.ac.jp/~smith/Lab.htm

22 May 2019

Laboratory philosophy...

Supercritical Fluid Technology
System Development Division

SMITH LAB.

Do it for fun...

Share...

Learn...

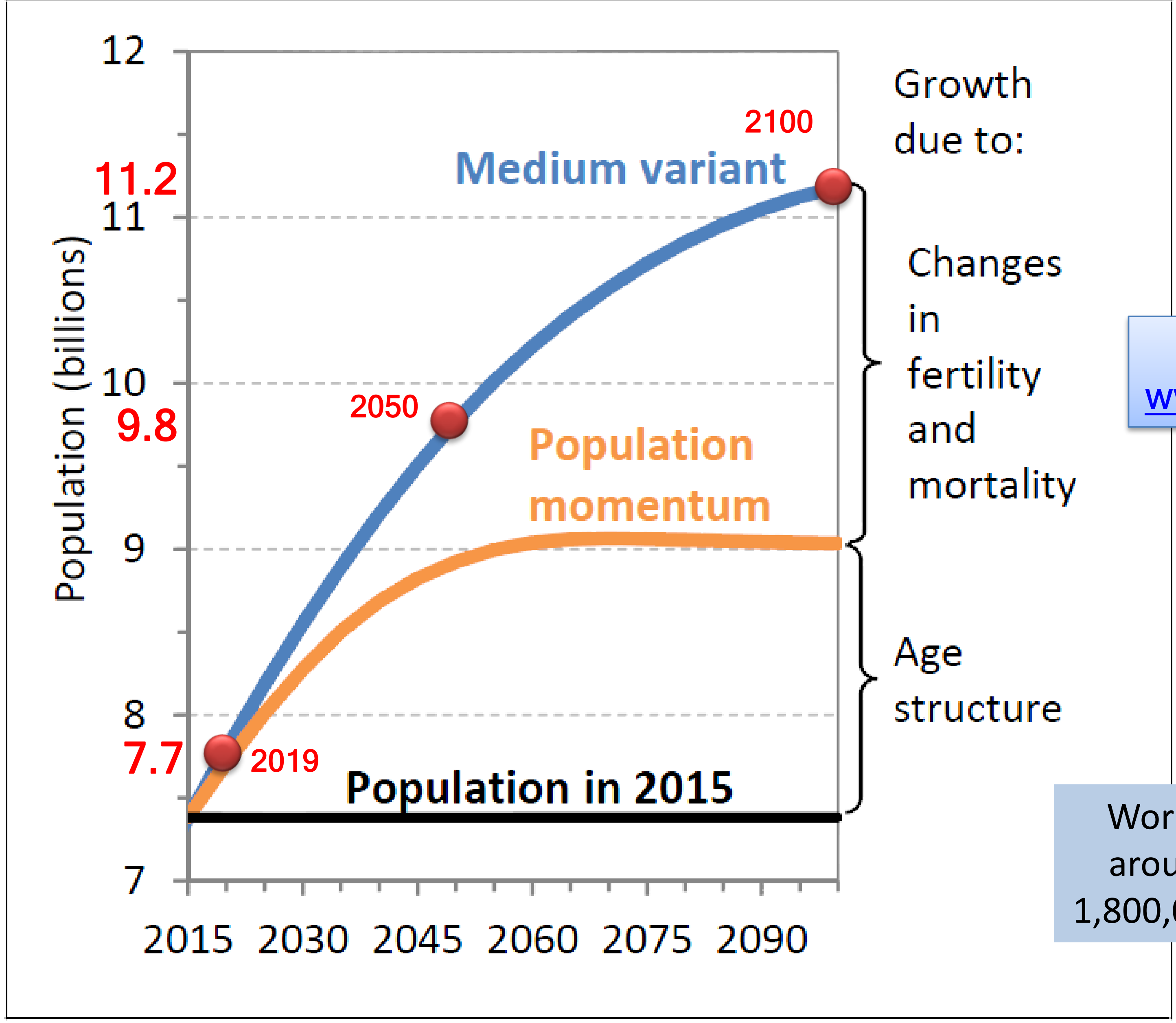
Improve it...

Outline

1. World population and CO_2 emissions
2. World oil supply and demand
3. Carbon-negative oil
4. Supercritical CO_2
5. Green chemical processes
6. Concluding Remarks

1. World population and CO_2 emissions

Figure 1. Projected size of the world's population, medium and momentum variants, 2015-2100



Source (2019): www.un.org/develop

World population around 1918 was 1,800,000,000 people

World Population in 2050

SMITH LAB.!
ercritical Fluid Technology
ystem Development Division

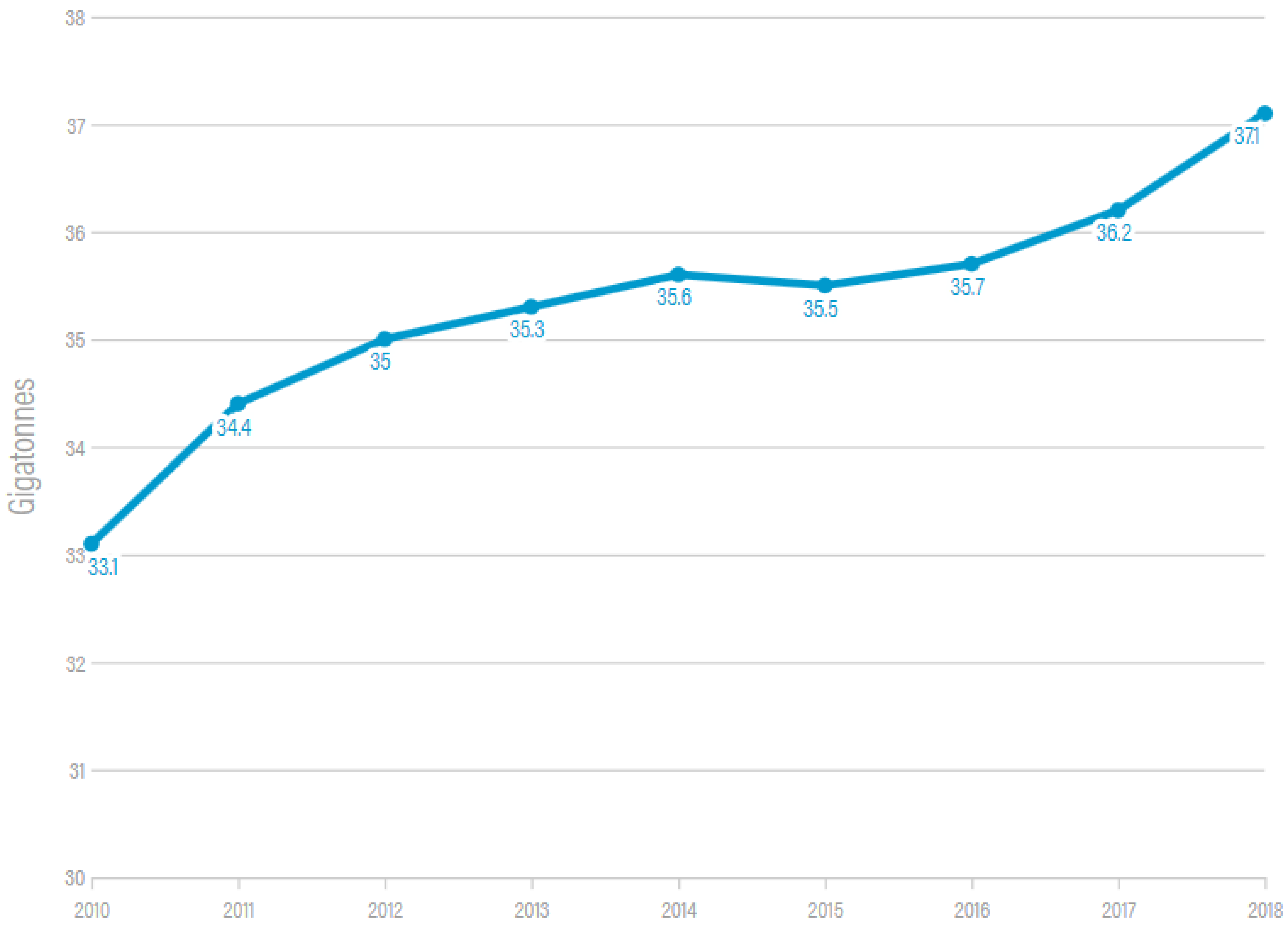
Rank	*Country or area*	*Population in 2050 (millions)*
1.	India	1 659
2.	China	1 364
3.	Nigeria	411
4.	United States of America	390
5.	Indonesia	322
6.	Pakistan	307
7.	Brazil	233
8.	Bangladesh	202
9.	Dem. Republic of the Congo	197
10.	Ethiopia	191

Source (2019):
www.un.org/develop

11.	Mexico	164
12.	Egypt	153
13.	Philippines	151
14.	United Republic of Tanzania	138
15.	Russian Federation	133
16.	Viet Nam	115
17.	Japan	109
18.	Uganda	106
19.	Turkey	96
20.	Kenya	95

Carbon Dioxide Emissions Back on the Rise

CO2 emissions from fossil fuel energy sources

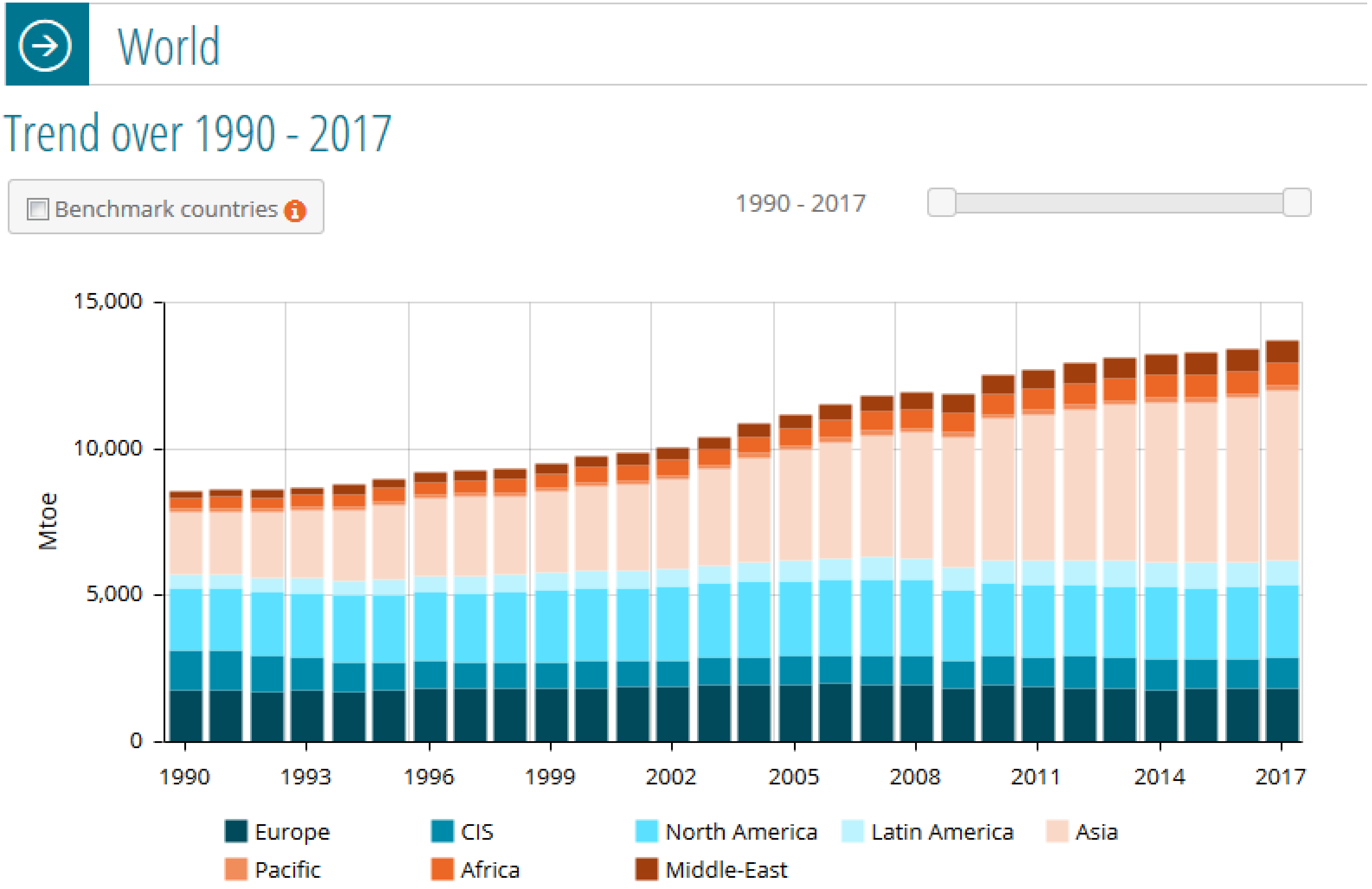


Source: Global Carbon Project

WORLD RESOURCES INSTITUTE

2. World oil supply and demand


OIL (WTI) PRICE COMMODITY
ADD
SHARE
63.39 USD 0.68 (1.08%) 06:42:00 PM MI Indication*
Prev. Close 62.71
Open 62.93
Day Low 62.93
Day High 63.60
52 Week Low 42.36
52 Week High 76.90
63.39
63.39
INTRADAY 1W 1M 3M 6M YTD 1Y 3Y 5Y 10Y MAX
INDICATORS
CHART OPTIONS
65.00
62.50
60.00
57.50
55.00
52.50
50.00
47.50
45.00
42.50
15.00%
11.16%
5.00%
0.00%
-5.00%
-10.00%
-15.00%
-20.00%
-25.00%
Dec 14 2019 14 Feb 14 Mar 14 Apr 14 May 14



Energy Consumption

Oil: 32 %

Gas: 22 %

Coal: 27 %

Biomass: 10 %

Electricity: 9 %

https://yearbook.enerdata.net/total-energy/world-consumption-statistics.html

If 1 L of oil (gas/petrol) is totally combusted, how much CO_2 is emitted? (ρ_{oil} = 800 kg/m^3)

If 1 L of oil (gas/petrol) is totally combusted, how much CO_2 is emitted? (ρ_{oil} = 800 kg/m^3)

$$1\ \text{L} \times \frac{1\ \text{m}^3}{1000\ \text{L}} \times \frac{800\ \text{kg}}{\text{m}^3} \times 0.85\ \text{C (in oil)} = 0.68\ \text{kg C} \times \frac{1\ \text{mol}}{12\ \text{g}} = 0.0566\ \text{kmol C}$$

$$1\ \text{mol C} + 1\ \text{mol O}_2 = 1\ \text{mol CO}_2$$

$$0.0566\ \text{kmol O}_2 \times \frac{32\ \text{g}}{\text{mol}} = 1.81\ \text{kg O}_2$$

$$\text{kg CO}_2 = 0.68\ \text{kg C} + 1.81\ \text{kg O}_2 = 2.5\ \text{kg CO}_2$$

If 1 barrel of oil (159 L) is totally combusted, how much CO_2 is emitted?

How much CO_2 is emitted if 1 toe (tonne of oil equivalent) is totally combusted? (1 toe = 7.33 barrels of oil)

In 2017, CO_2 emissions were 36.2 Gigatonnes. How many Mtoe does this correspond to?

If 1 barrel of oil (159 L) is totally combusted, how much CO_2 is emitted?

Answer: about 400 kg CO_2

How much CO_2 is emitted if 1 toe (tonne of oil equivalent) is totally combusted?

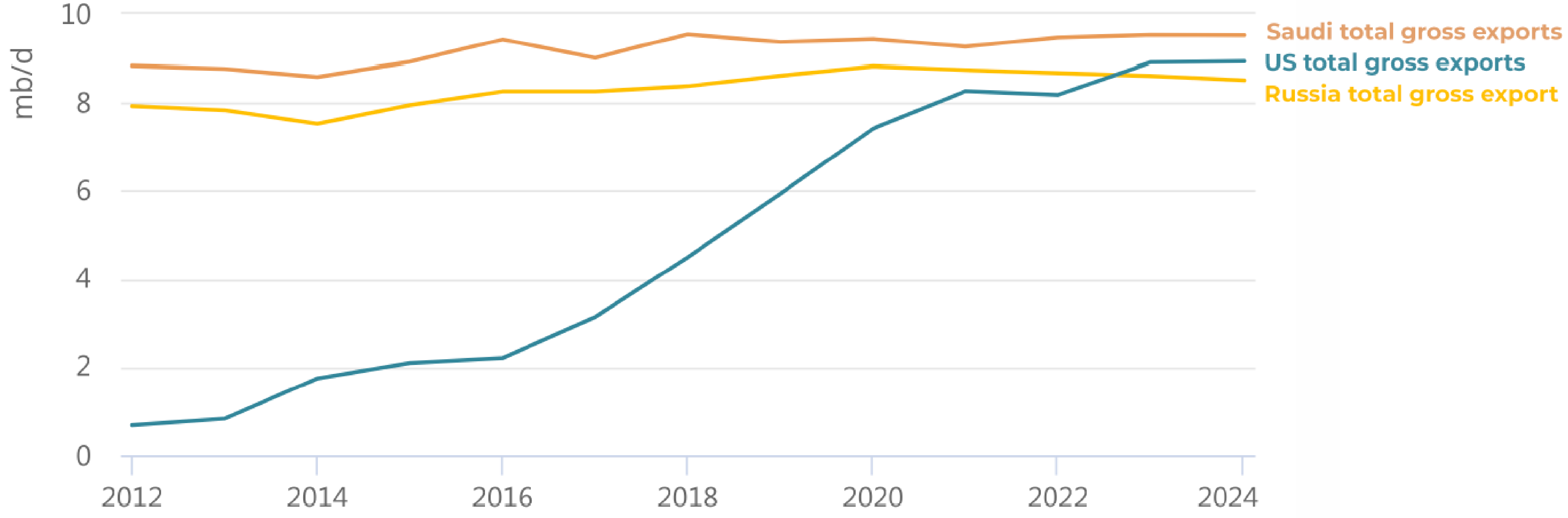
(1 toe = 7.33 barrels of oil)

Answer: about 2900 kg CO_2

In 2017, CO_2 emissions were 36.2 Gigatonnes. How many Mtoe does this correspond to?

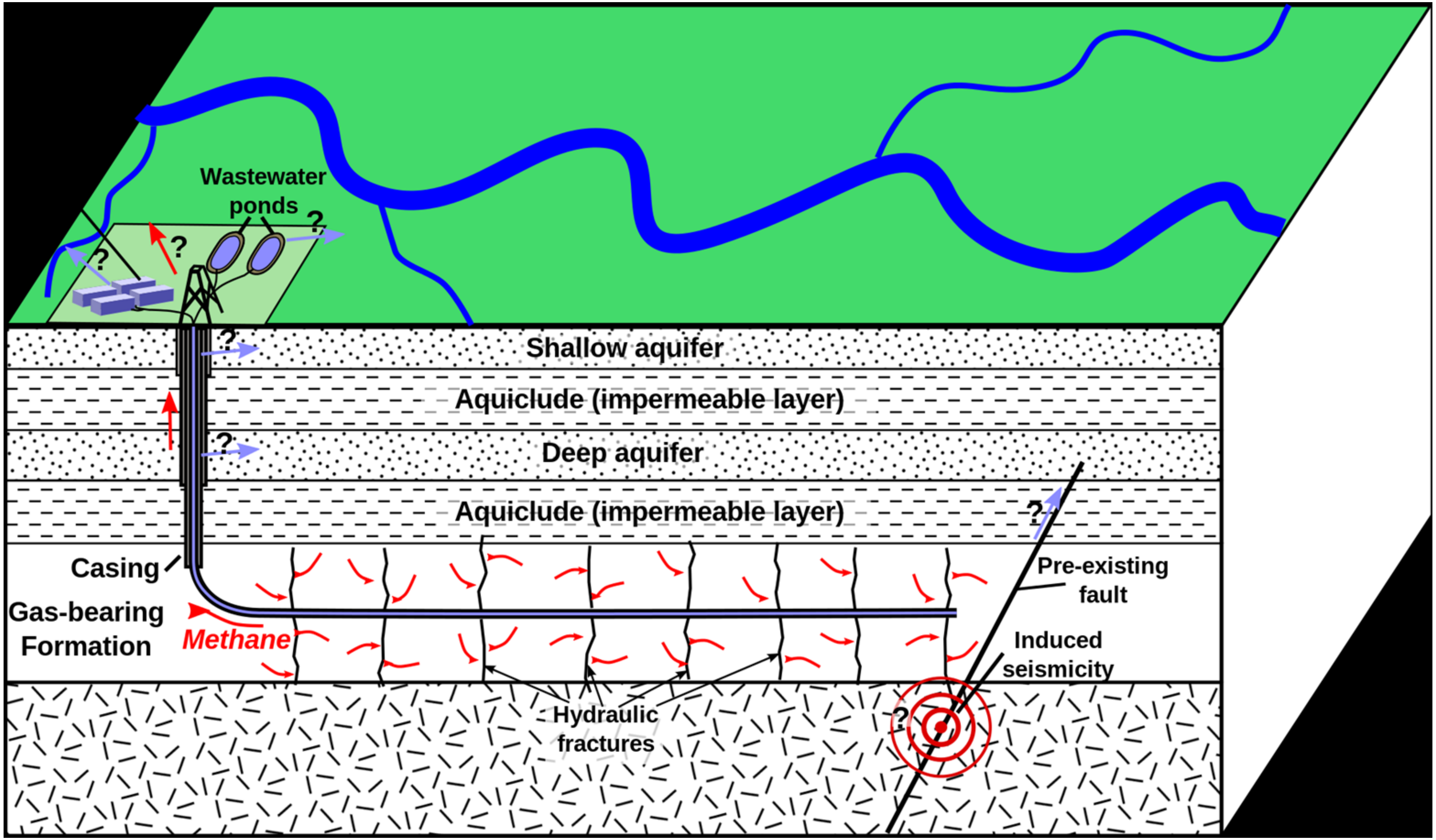
Answer: about 12483 Mtoe

US gross exports overtake Russia, catch up with Saudi Arabia



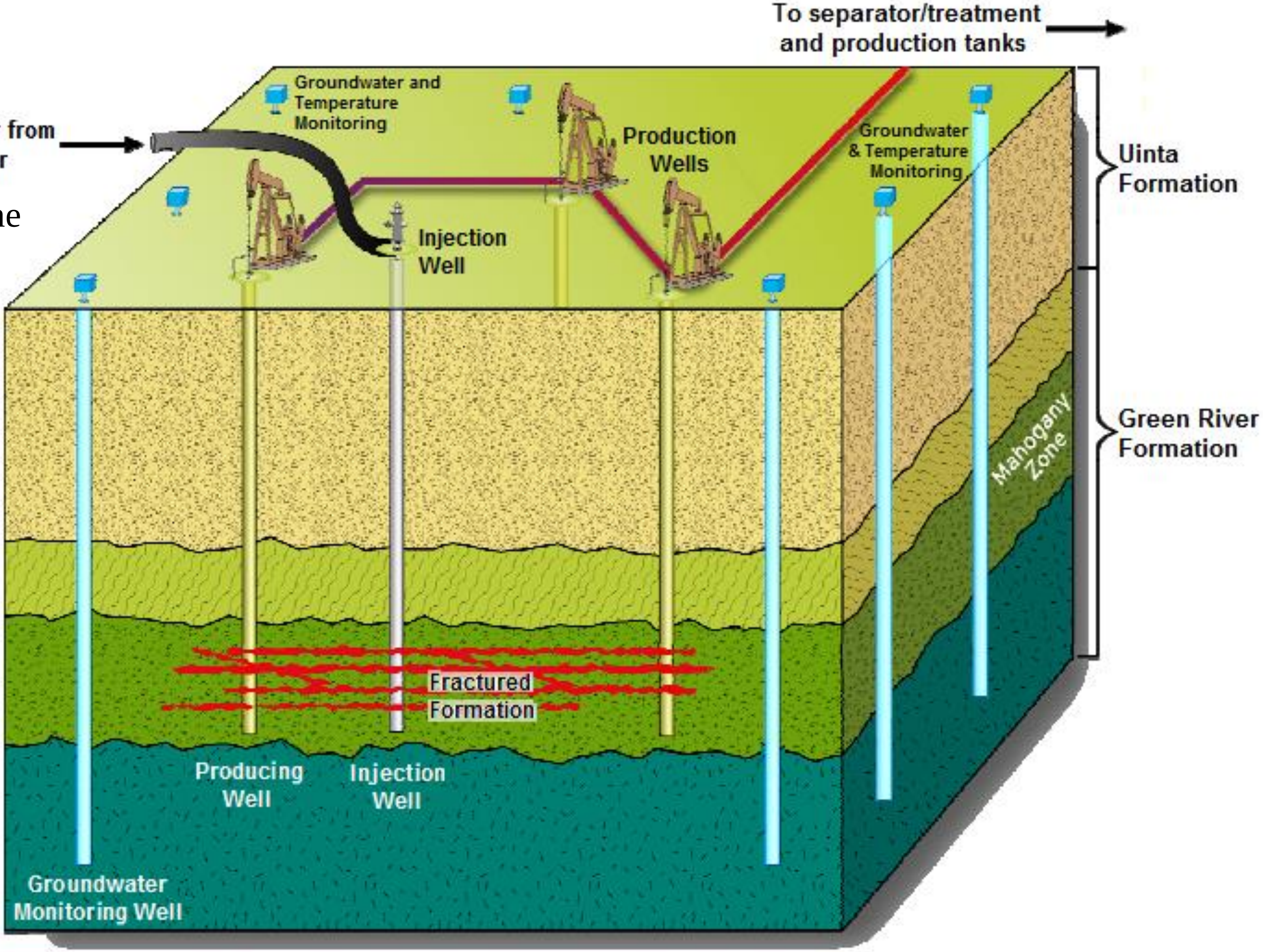
US is *net* oil exporter in 2021 after 75 years of import dependency. US exports add to market flexibility

Hydraulic fracturing (Fracking) for obtaining shale gas



Chevron CRUSH process for obtaining shale oil

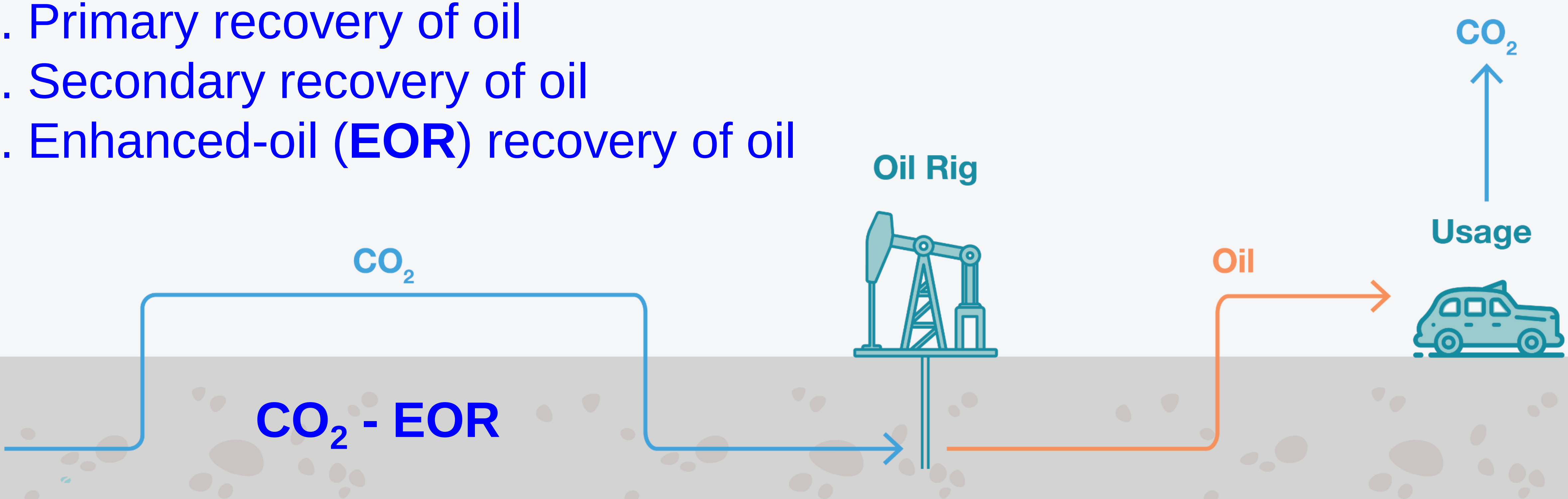
Chevron's technology for the
Recovery and
Upgrading of Oil from
SHale



3. Carbon-negative oil

Can we produce carbon-negative oil?

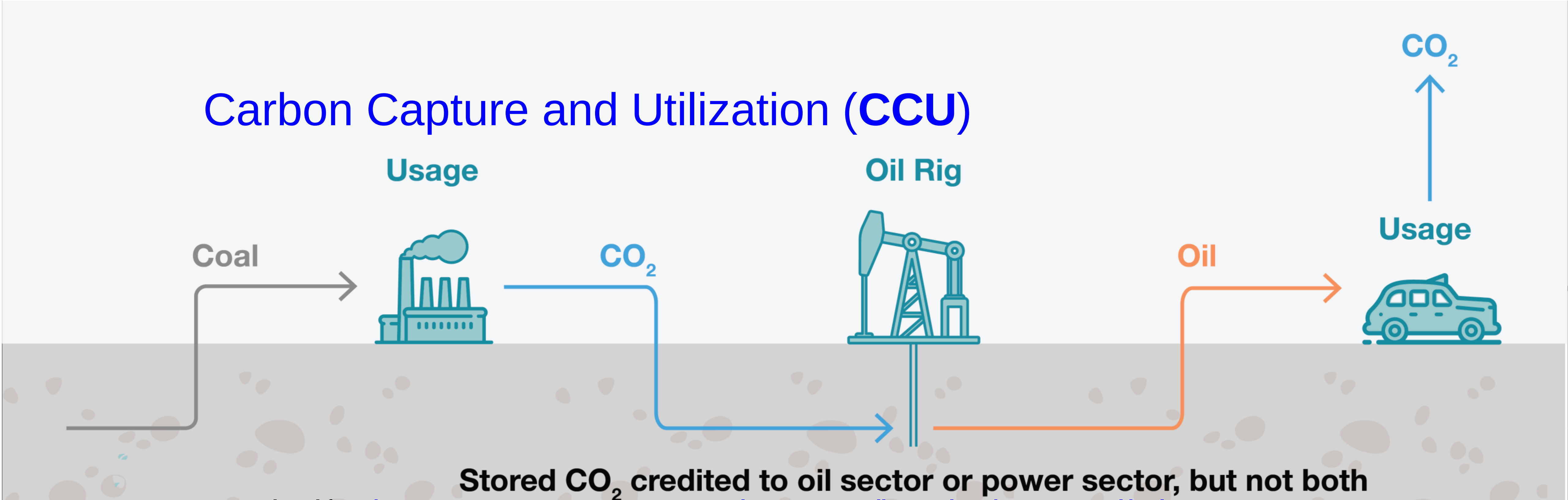
1. Primary recovery of oil
2. Secondary recovery of oil
3. Enhanced-oil (**EOR**) recovery of oil



Adapted from: https://www.iea.org/newsroom/news/2019/april/can-co2-eor-really-provide-carbon-negative-oil.html

Enhanced-oil recovery (EOR) - CO_2 aids in oil extraction

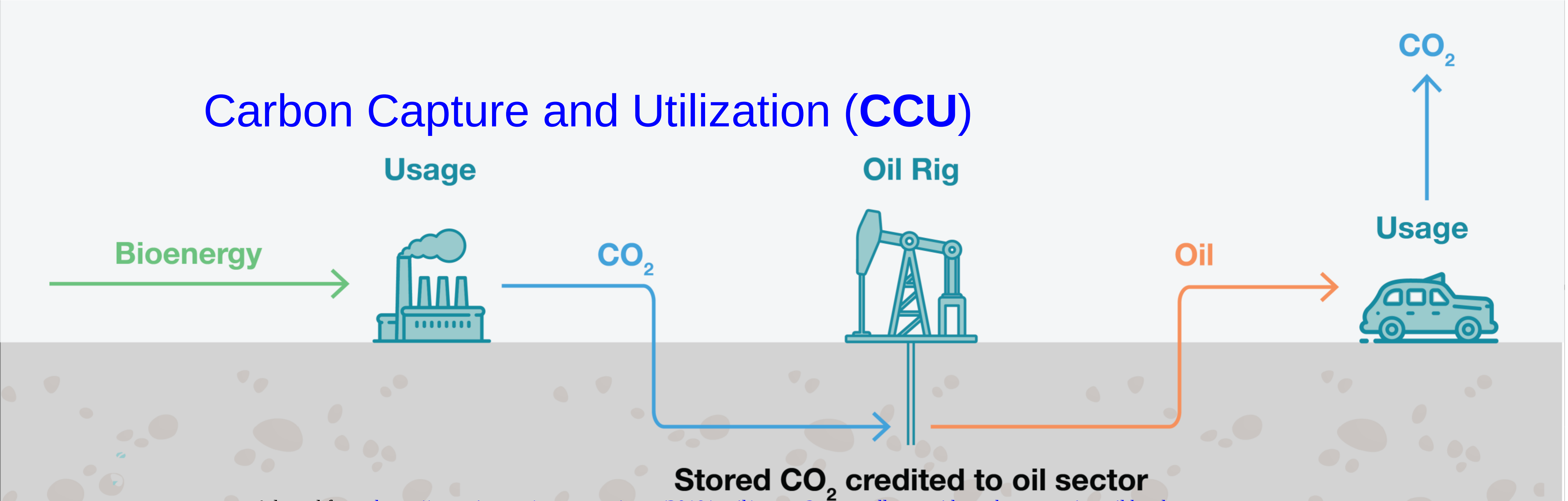
Can we produce carbon-negative oil?



Adapted from: https://www.iea.org/newsroom/news/2019/april/can-co2-eor-really-provide-carbon-negative-oil.html

CO_2 from coal combustion is used for CO_2 - EOR

Can we produce carbon-negative oil?



Adapted from: https://www.iea.org/newsroom/news/2019/april/can-co2-eor-really-provide-carbon-negative-oil.html

CO_2 from bioenergy is used for CO_2 - EOR

4. Supercritical CO_2

Introduction To Supercritical Fluids
A Spreadsheet-based Approach
Richard Smith, Hiroshi Inomata, Cor Peters
Elsevier, 2013

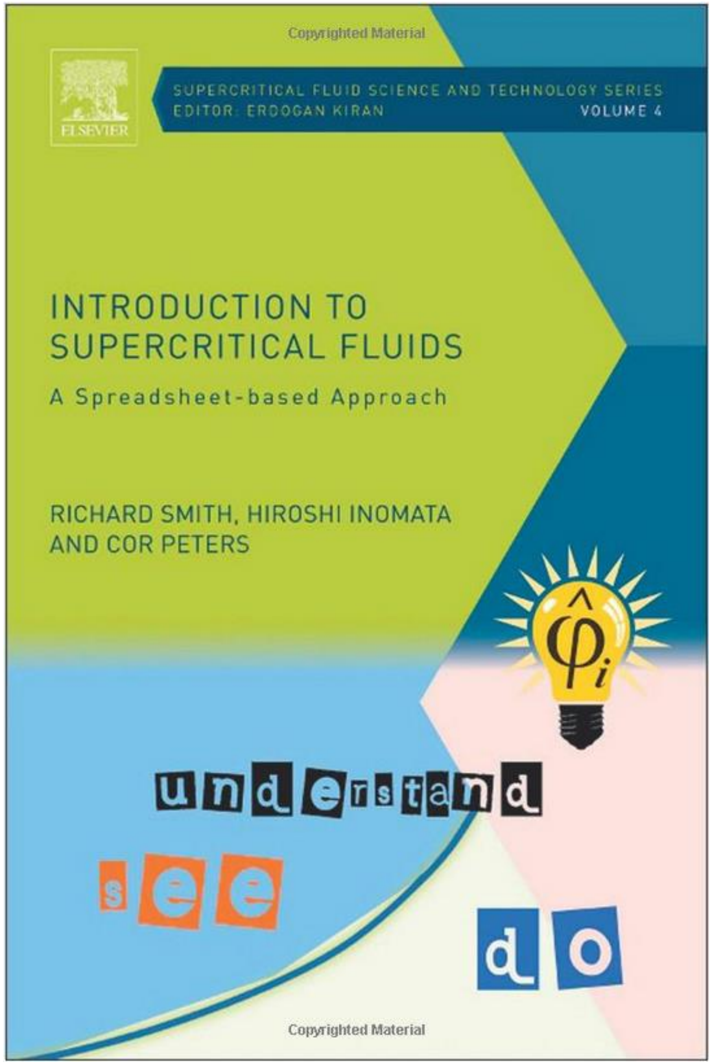
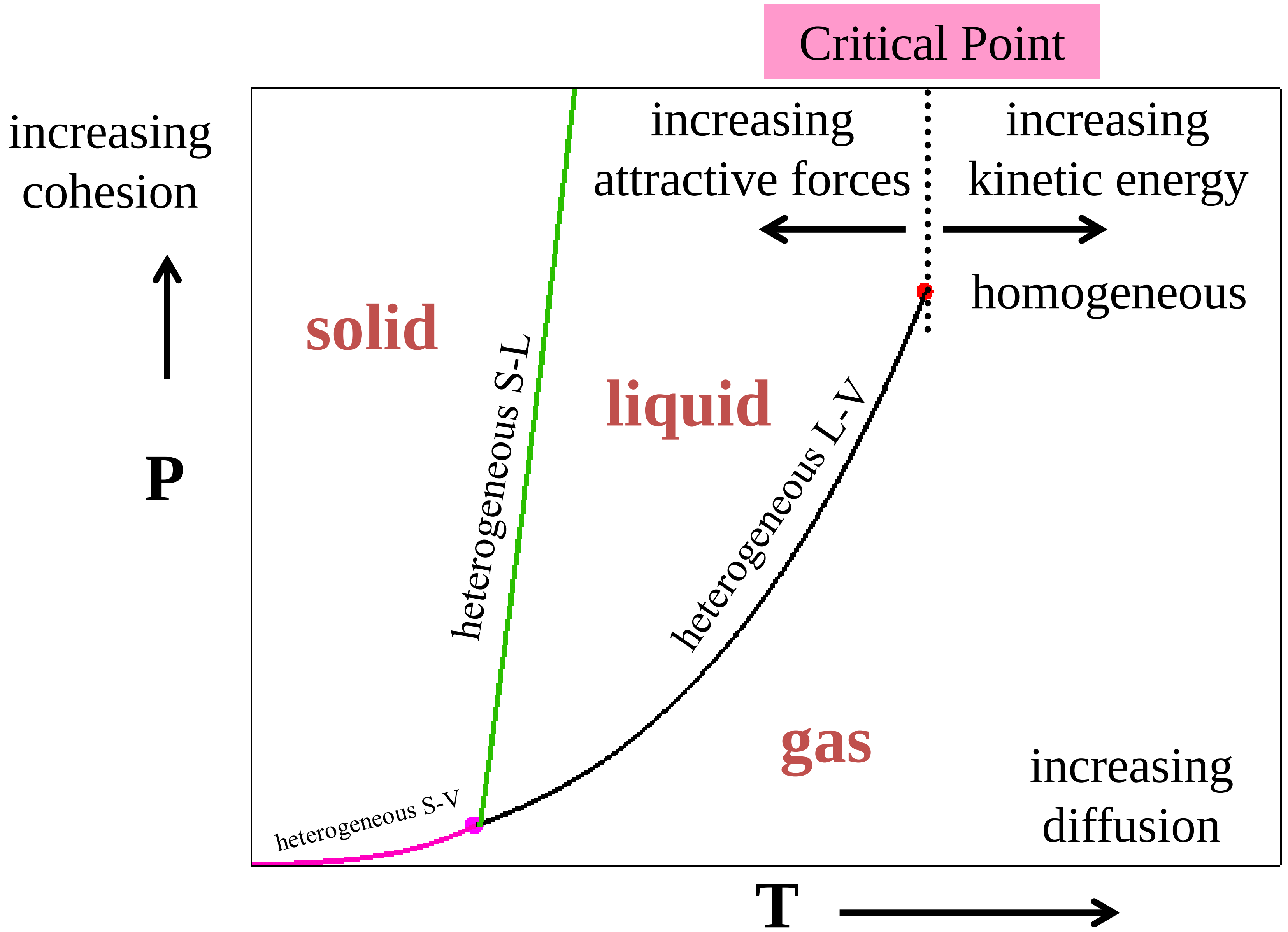


Table of Contents

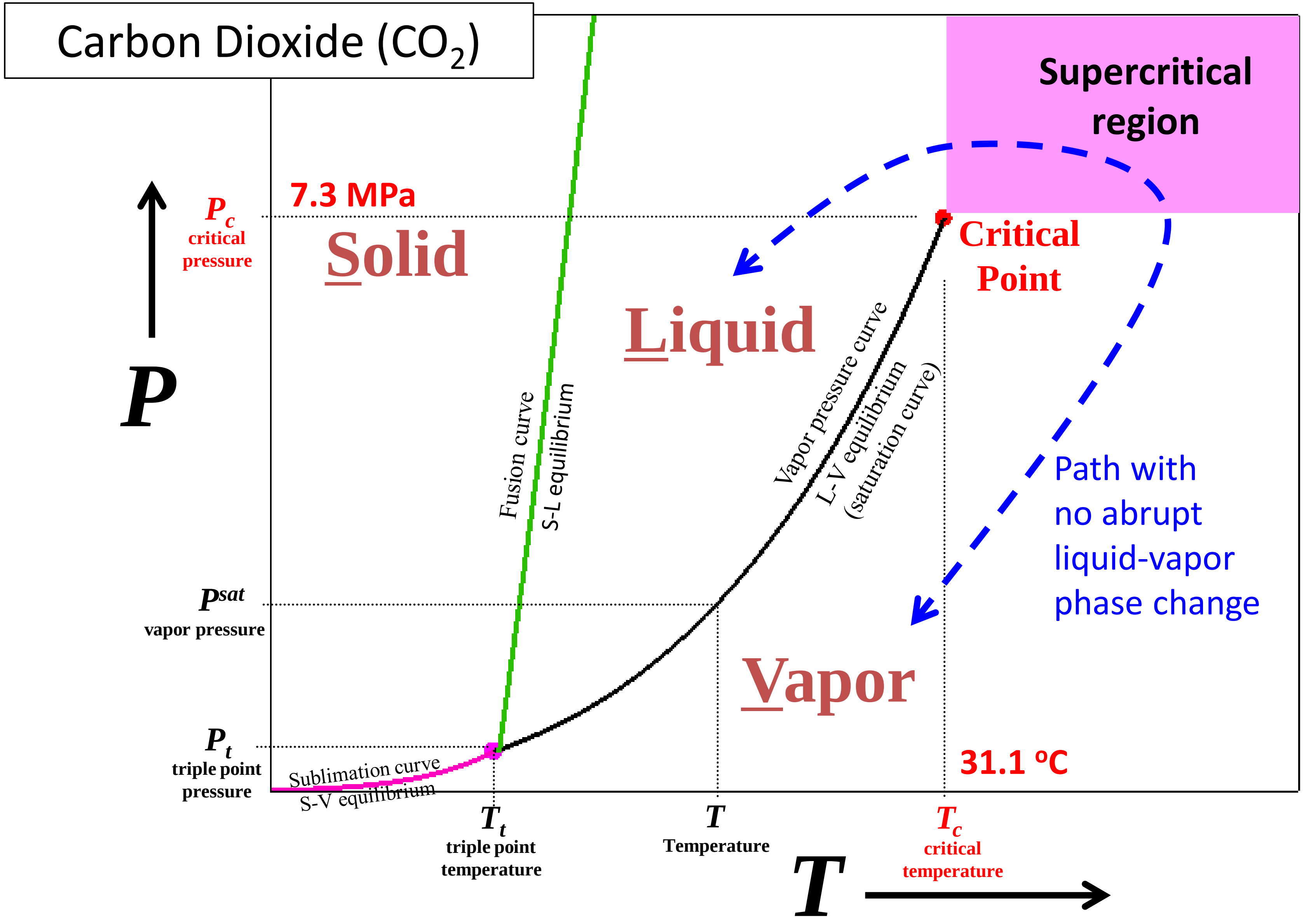
* Print
* Print/eBook
* Print/Kindle

http://store.elsevier.com/product.jsp?isbn=9780444522153&pagename=search

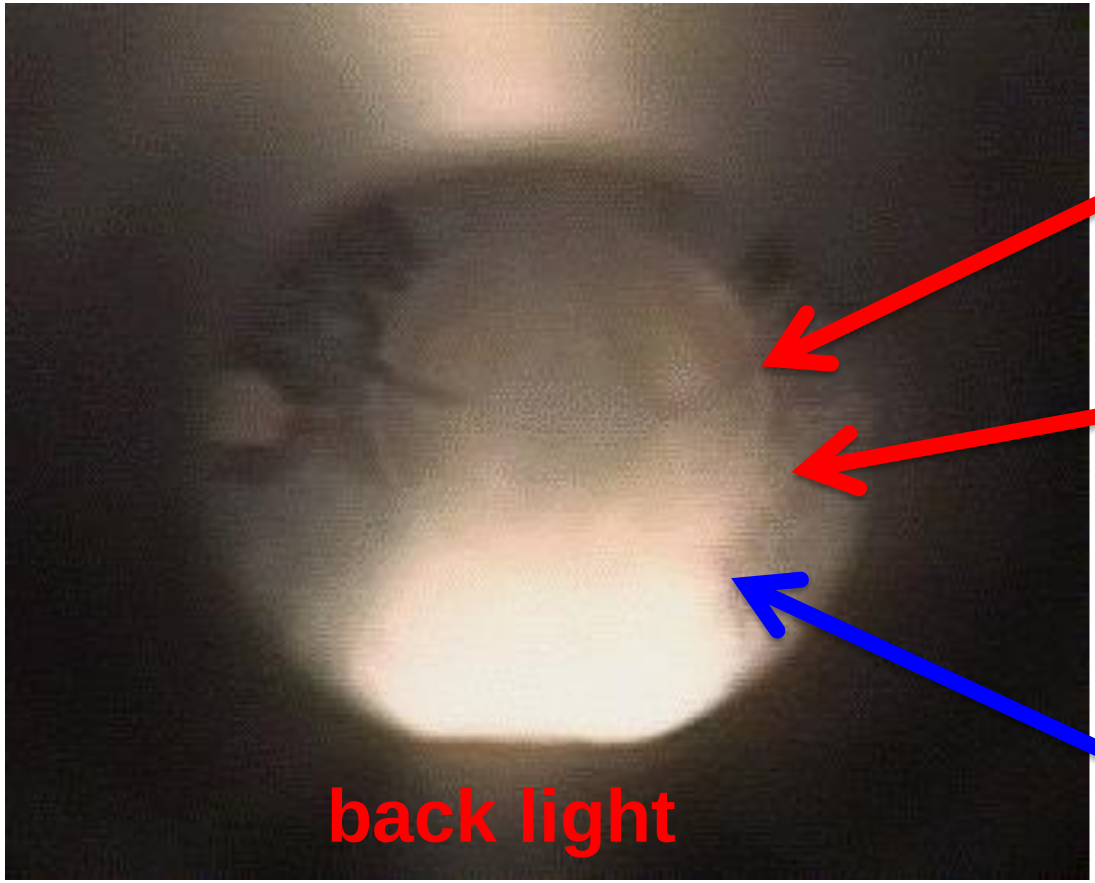
Pressure-Temperature Diagram



Pressure-Temperature Diagram



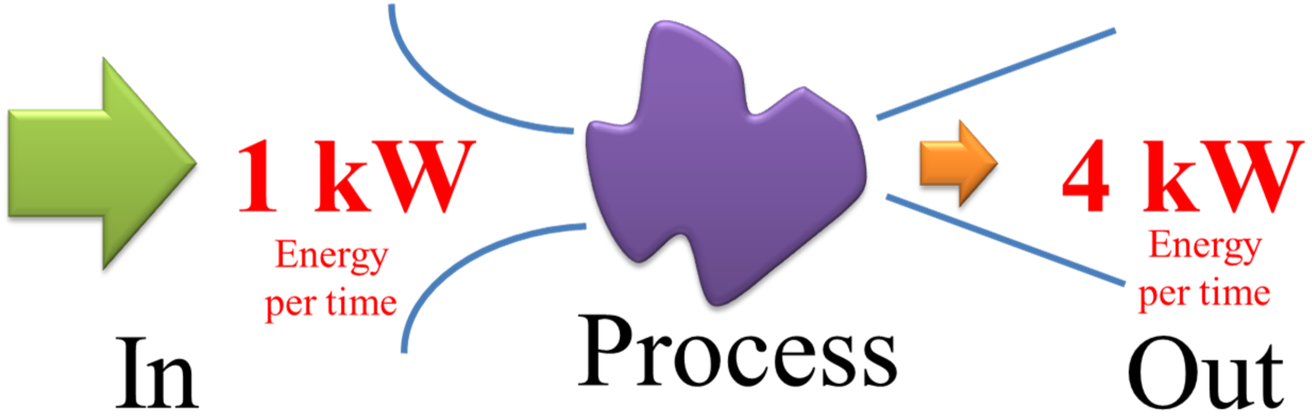
Supercritical CO_2 circulating in a cell. An external temperature gradient causes the supercritical phase to circulate without mechanical devices.



S. Yoshikawa, R.L. Smith Jr, H. Inomata, Y. Matsumura, K. Arai, **Performance of a Natural Convection Circulation System for Supercritical Fluids**, **Journal of Supercritical Fluids, 36 (2005) 70-80.**

Group Question – energy of a device

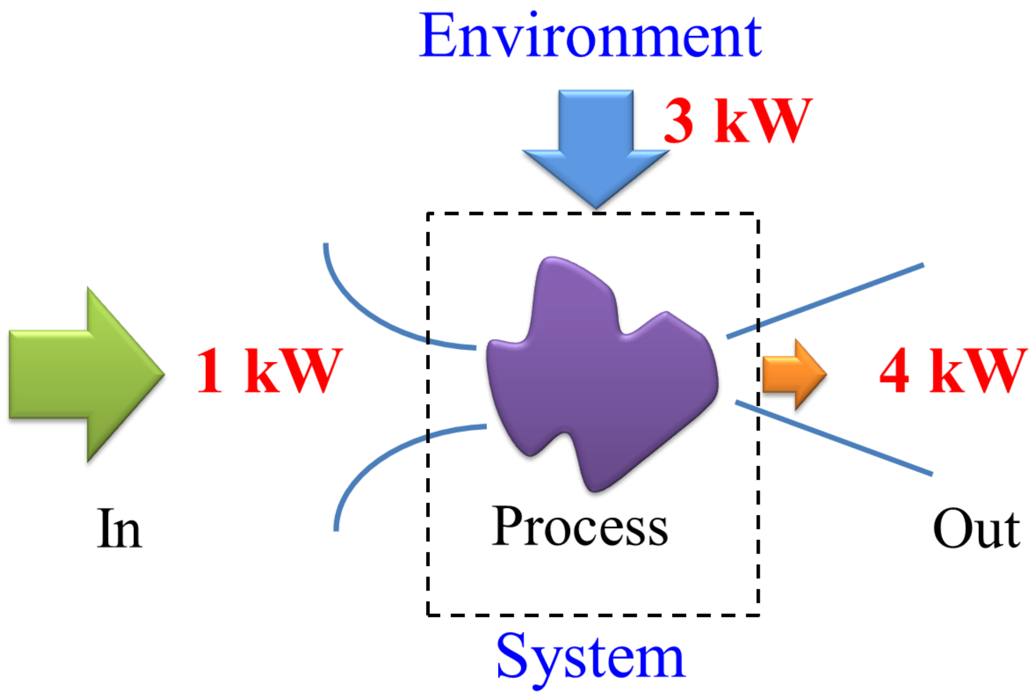
A salesperson claims that an "energy multiplying" device has just been invented that can continuously multiply energy without the need for batteries, solar, wave or wind energy. The device is shown below:



Choose one of the answers below:

(1) Impossible. State why.
(2) Possible. State why.

Answer: always consider the environment



Answer: Possible! The system uses the energy of the environment to achieve efficient conversion of electrical work to thermal energy.

Transcritical CO_2 Heat pump

自然冷媒ヒートポンプ給湯機

EcoCute was marketed in Japan in May 2001. As of 2009, 2 million units have been sold by more than 26 manufacturers.

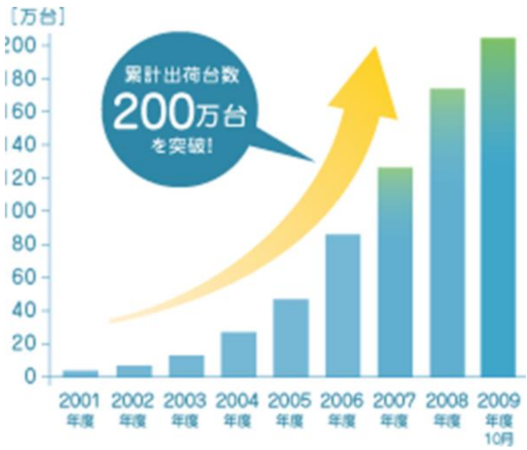
Update

2014 More than 4 million units installed (Japan)

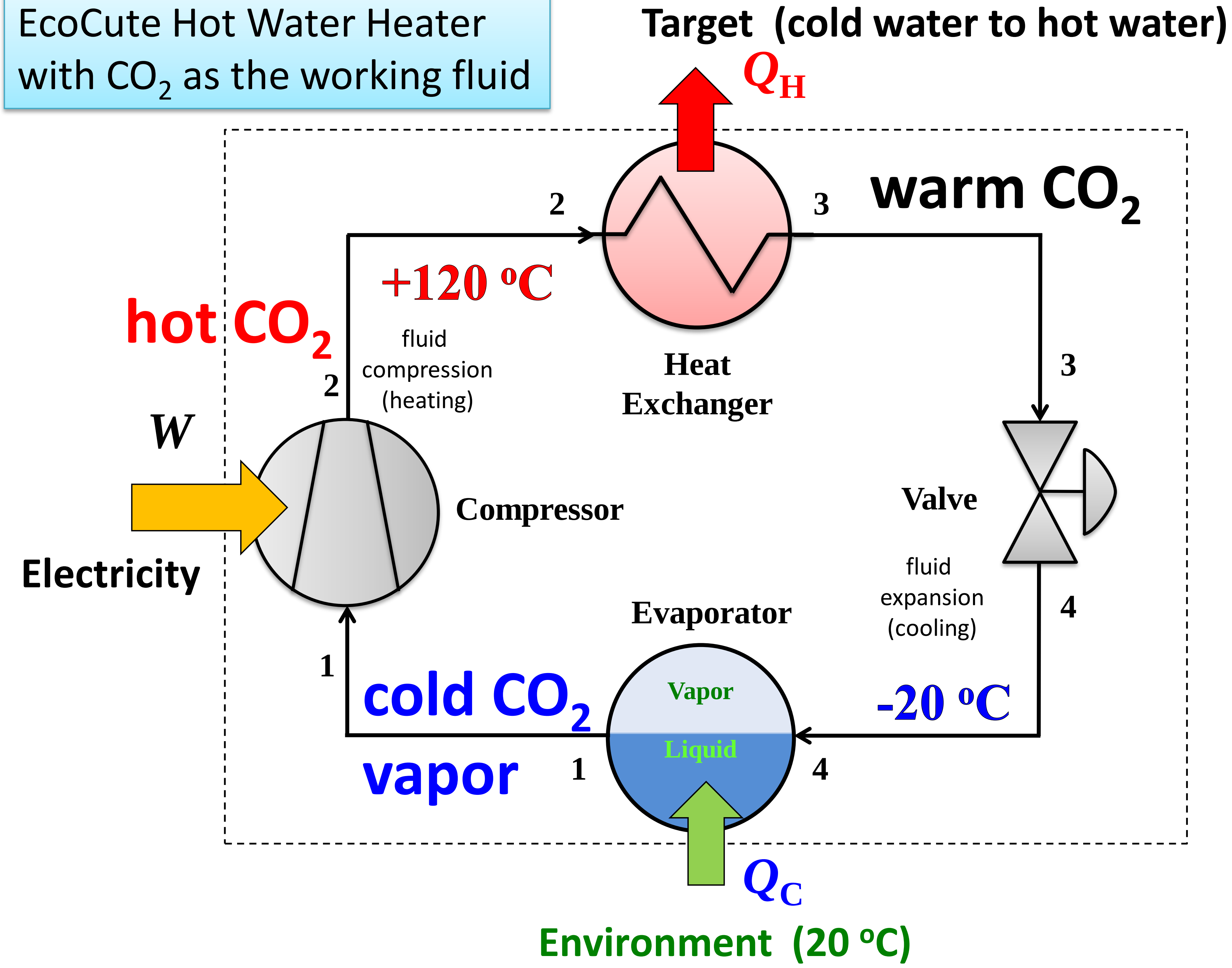
400,000 to 500,000 units installed/year

100 °C 10 MPa

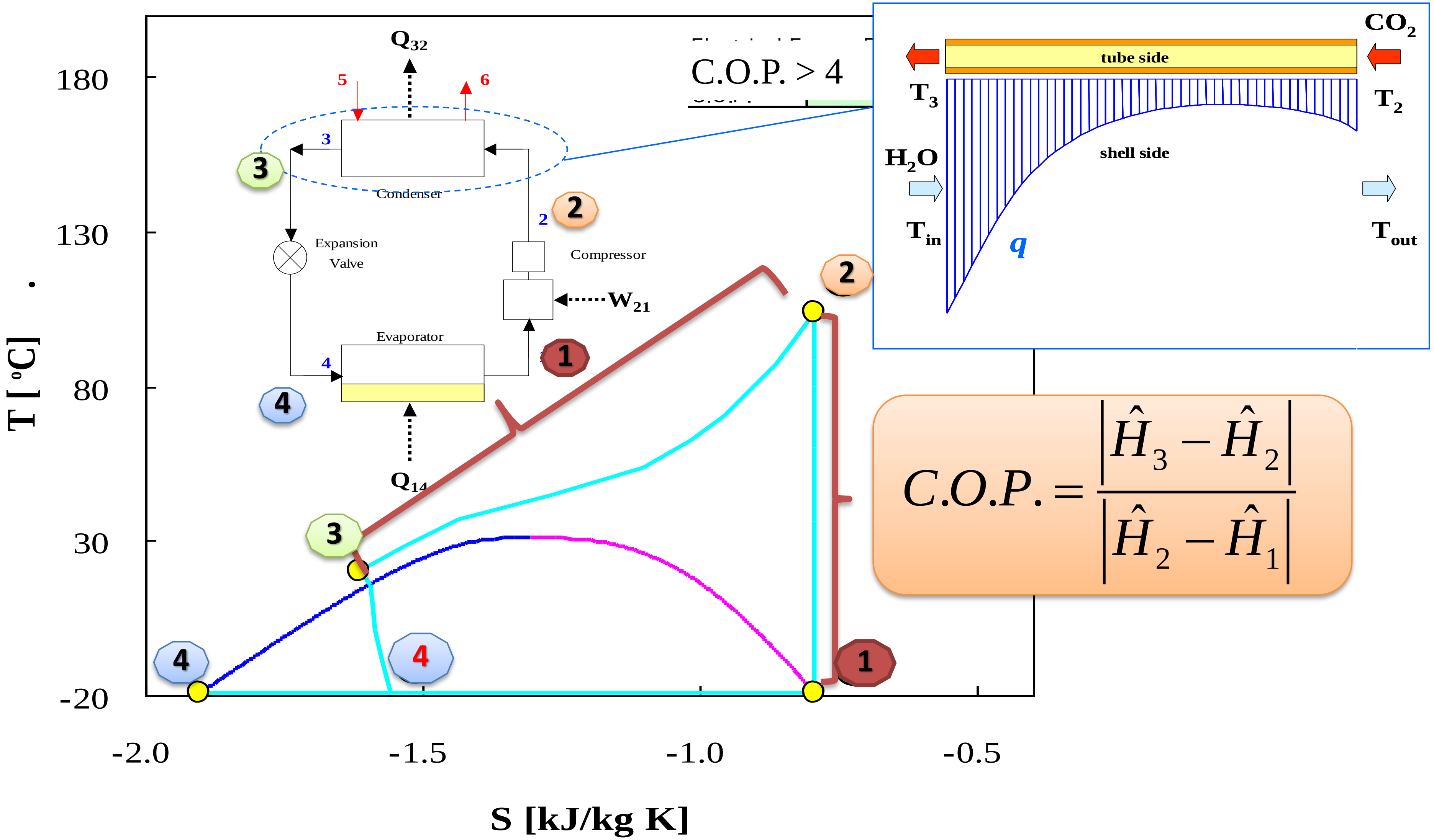
To produce 90 °C hot water, an EcoCute consumes 66% less energy than an electric water heater, and costs 80% less than heating water via city gas in Japan. The EcoCute results in more than 50% reductions in CO_2 emissions



EcoCute Hot Water Heater with CO_2 as the working fluid



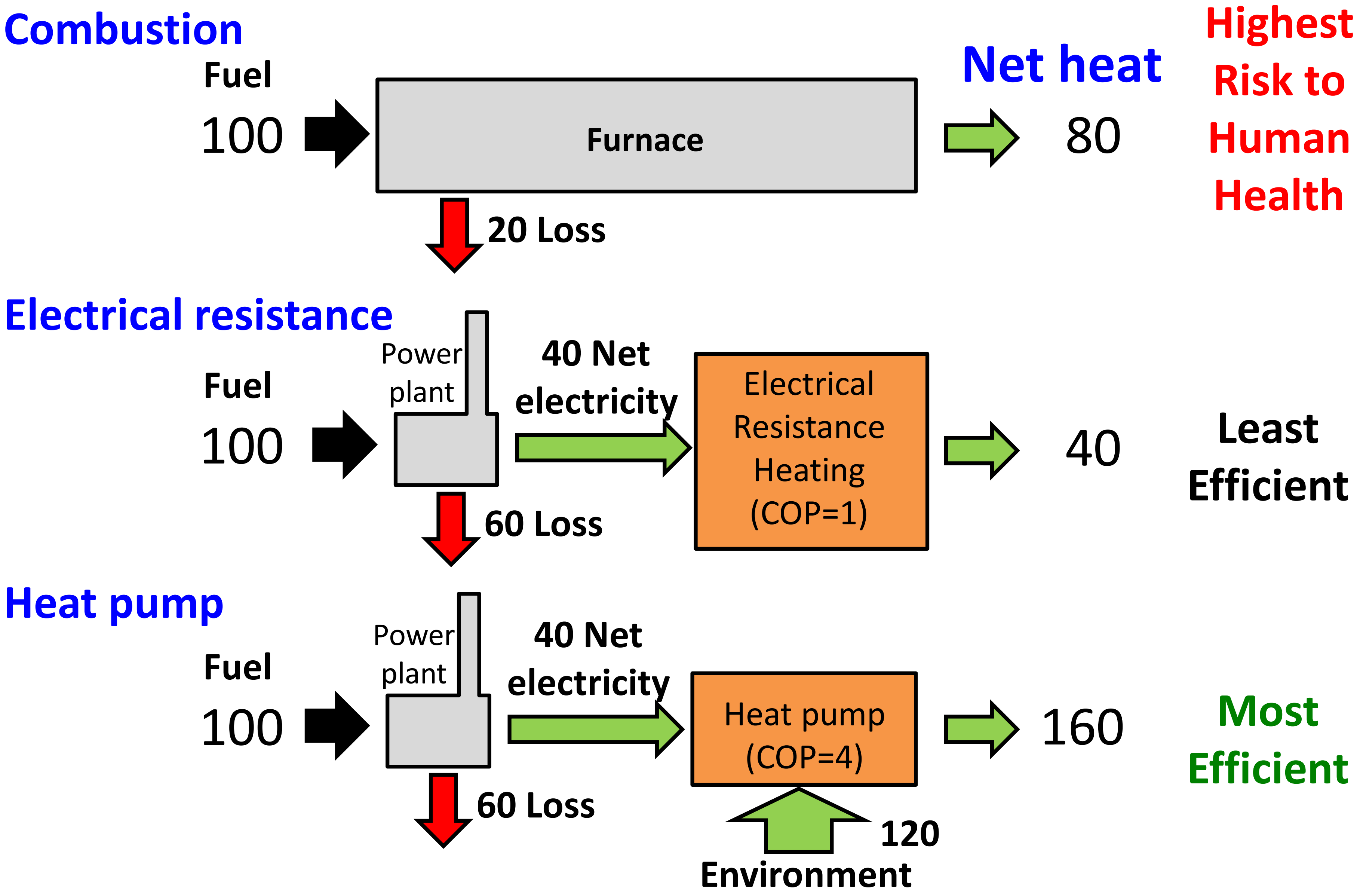
Energy systems-transcritical heating cycles



$$C.O.P. = \frac{\left|\hat{H}_3 - \hat{H}_2\right|}{\left|\hat{H}_2 - \hat{H}_1\right|}$$

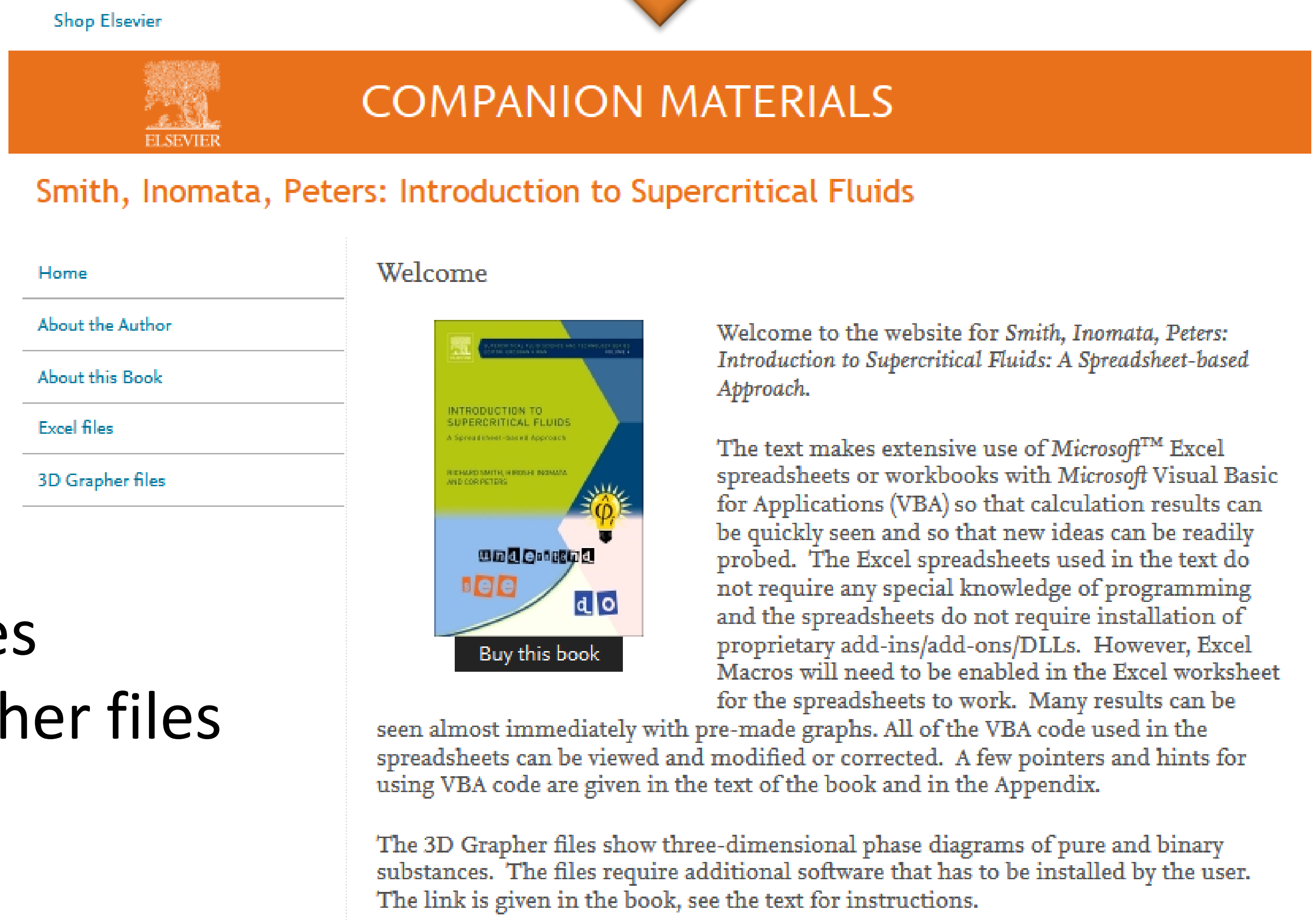
Transcritical cycles avoid energy-inefficient boiling or condensation

Comparison of methods to make hot water



Access to the programs

http://booksite.elsevier.com/9780444522153/


Shop Elsevier

ELSEVIER

COMPANION MATERIALS

Smith, Inomata, Peters: Introduction to Supercritical Fluids

- Home
- About the Author
- About this Book
- Excel files
- 3D Grapher files

Welcome

Buy this book

Welcome to the website for *Smith, Inomata, Peters: Introduction to Supercritical Fluids: A Spreadsheet-based Approach*.

The text makes extensive use of *Microsoft*™ Excel spreadsheets or workbooks with *Microsoft* Visual Basic for Applications (VBA) so that calculation results can be quickly seen and so that new ideas can be readily probed. The Excel spreadsheets used in the text do not require any special knowledge of programming and the spreadsheets do not require installation of proprietary add-ins/add-ons/DLLs. However, Excel Macros will need to be enabled in the Excel worksheet for the spreadsheets to work. Many results can be seen almost immediately with pre-made graphs. All of the VBA code used in the spreadsheets can be viewed and modified or corrected. A few pointers and hints for using VBA code are given in the text of the book and in the Appendix.

The 3D Grapher files show three-dimensional phase diagrams of pure and binary substances. The files require additional software that has to be installed by the user. The link is given in the book, see the text for instructions.

Excel files

3D Grapher files

5. Green Chemical Processes

Environmental Impact

Risk = Hazard x Exposure

Martyn Poliakoff, Science 297, 807 (2002)

Traditional:	Minimize Exposure
Green:	Minimize Hazard

Metric: E-Factor

Environmental - Factor

$$\text{E-Factor} = \frac{\text{(Waste generated [kg])}}{\text{(Product produced [kg])}}$$

Industry	Product tons per year	Waste/ product ratio by weight
Oil refining	$10^6 - 10^8$	~0.1
Bulk chemicals	$10^4 - 10^6$	<1–5
Fine chemicals	$10^2 - 10^4$	5–50
Pharmaceuticals	$10^0 - 10^3$	25–>100

2 AUGUST 2002 VOL 297 SCIENCE www.sciencemag.org

Low waste per kg product → Oil refining

High waste per kg product → Pharmaceuticals

R.A. Sheldon, Chem & Ind,1997,12; 1992,903

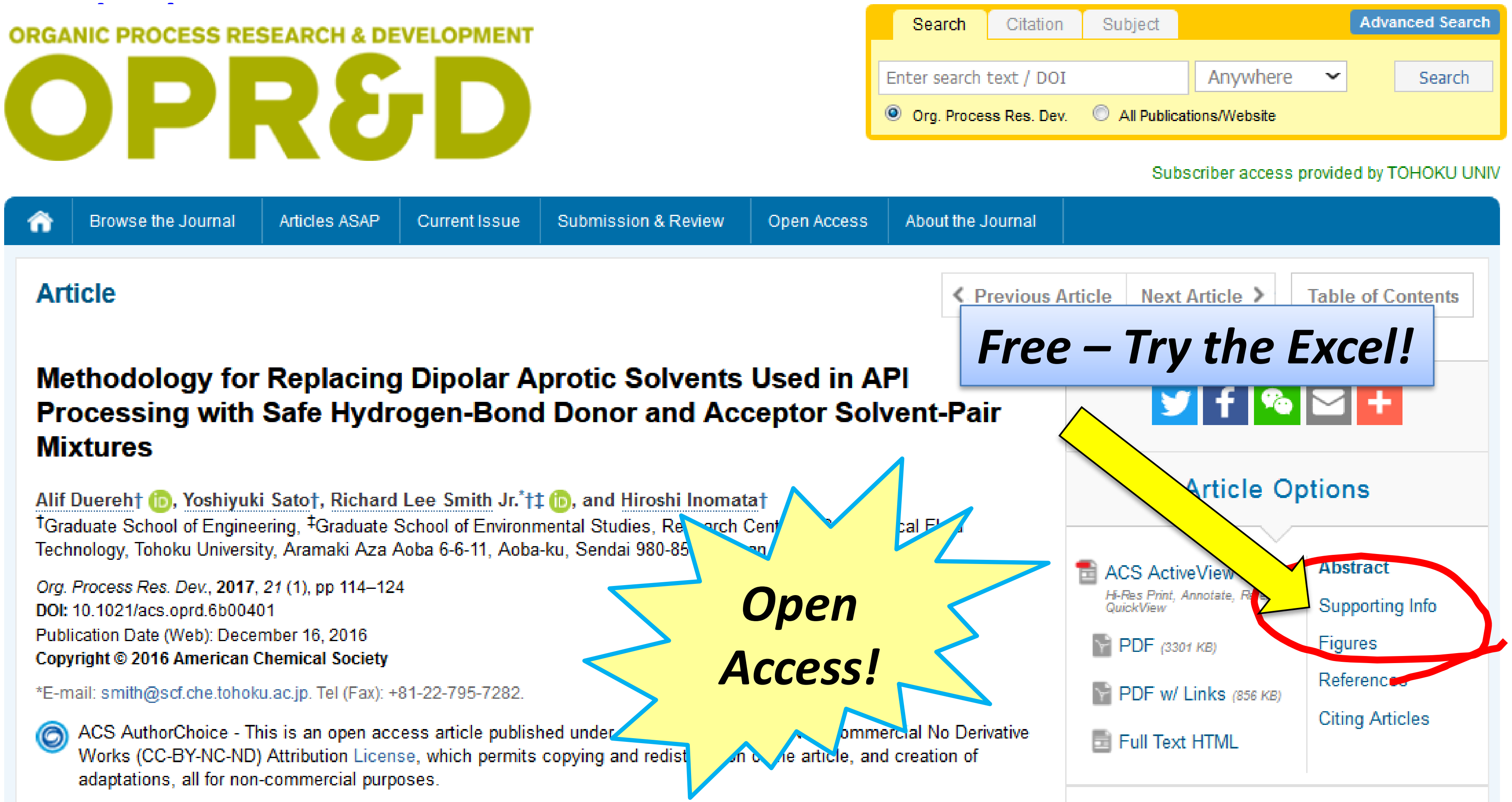
A large E-factor means much waste is generated for each kilogram of product

Solvent substitution methodology

- versatile
- safe
- economical
- widely applicable

Safe Solvent Mixtures
instead of
Hazardous Solvents

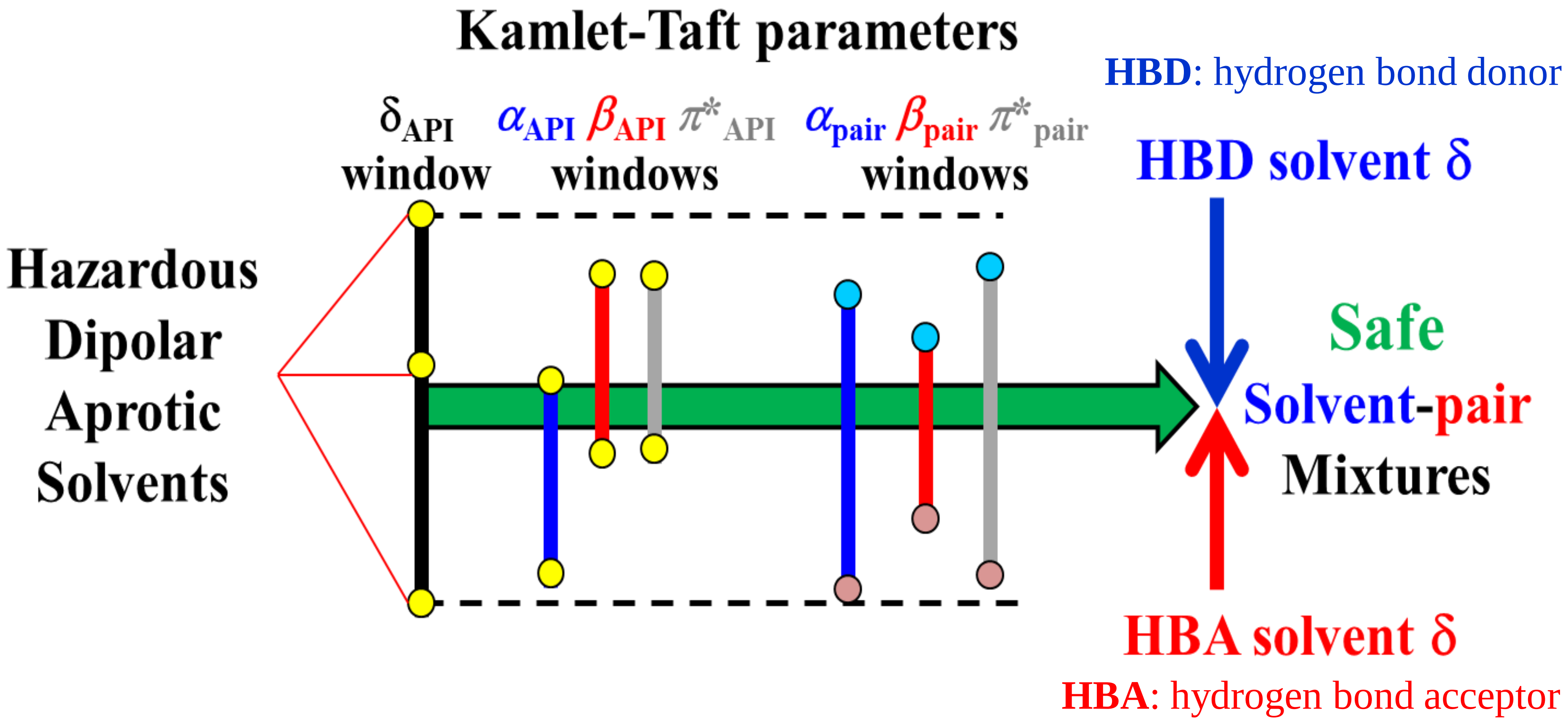
http://pubs.acs.org/doi/abs/10.1021/acs.op



Selected Publications on Properties, 2015-2017

Tohoku University/Smith Laboratory + Collaborators

Safe Mixed-solvents replace hazardous solvents



API: active pharmaceutical ingredient

A. Duereh, Y. Sato, R.L. Smith, H. Inomata, Methodology for replacing dipolar aprotic solvents used in API processing with safe hydrogen-bond donor and acceptor solvent-pair mixtures, Organic Process Research and Development 21(2017)114-124.

Catalytic ionic liquids

- efficient
- safe and noncorrosive
- economical
- easily recyclable

Selected Publications on Biomass, 2015-2017

Tohoku University/Smith Laboratory + Collaborators

Perfect recycle of homogeneous catalyst

H. Guo, A. Duereh, Y. Hiraga, T.M. Aida, X. Qi, R.L. Smith, Perfect recycle and mechanistic role of hydrogen sulfate ionic liquids as additive in ethanol for efficient conversion of carbohydrates into 5-ethoxymethylfurfural, Chemical Engineering Journal 323 (2017) 287-294.

Hydrogen-less methods

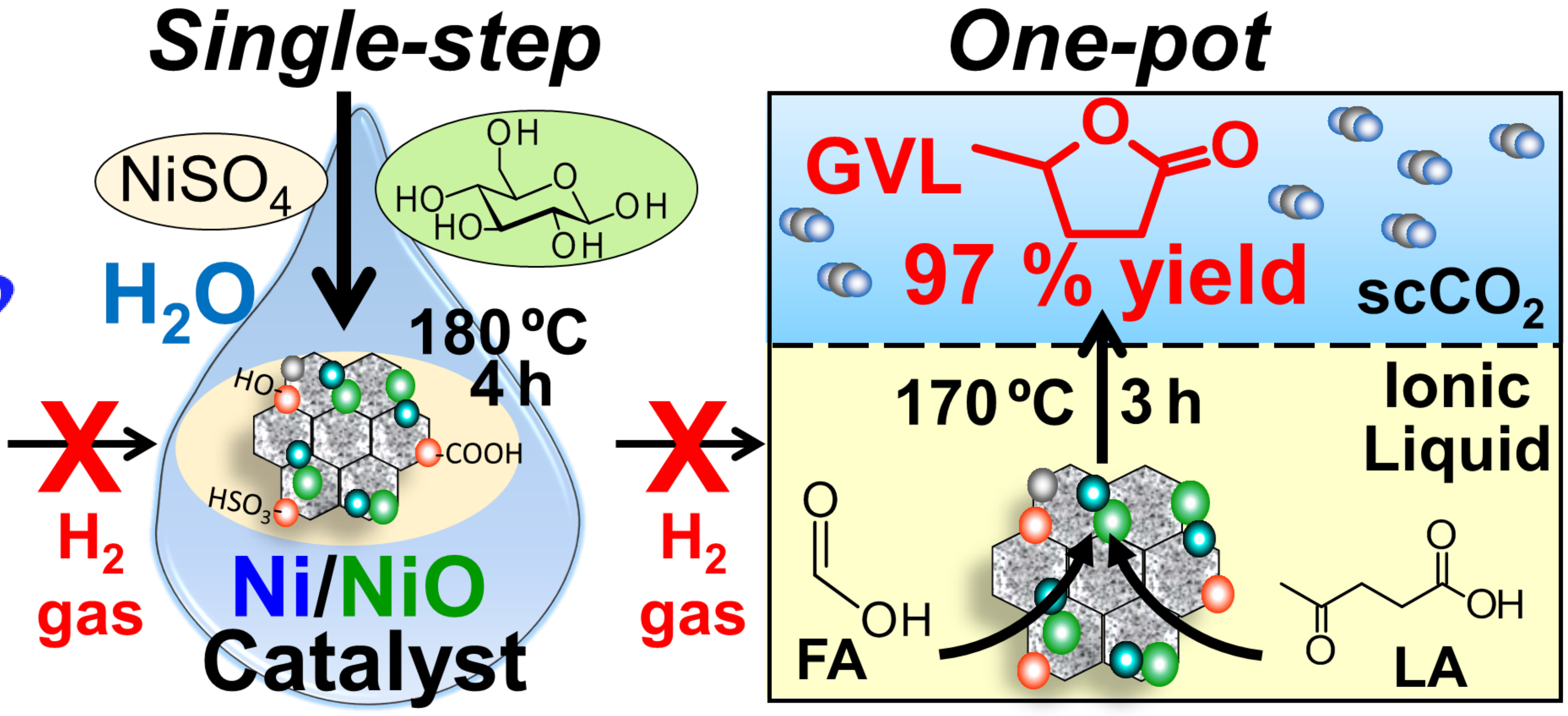
- efficient
- safe
- economical catalysts
- low-energy

Total synthesis of γ-valerolactone without H_2 gas

TOHOKU UNIVERSITY

RCSCF TOHOKU University

NANKAI UNIVERSITY 1919

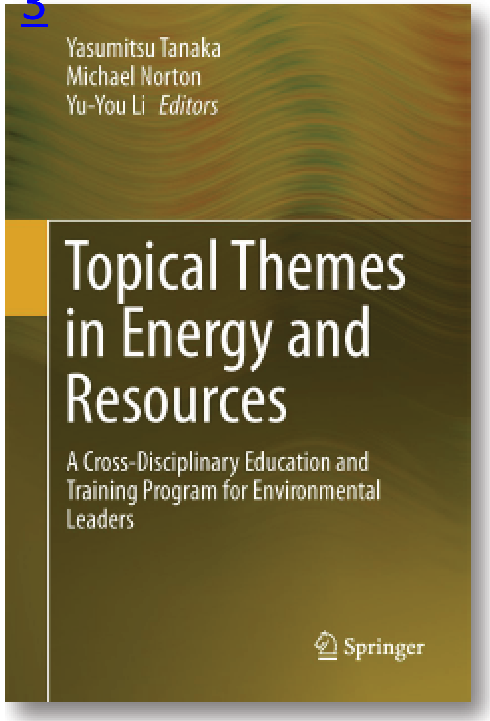


H. Guo, Y. Hiraga, X. Qi, R. L. Smith, Hydrogen Gas-Free Processes for Single-Step Preparation of Transition-Metal Bifunctional Catalysts and One-Pot γ-Valerolactone Synthesis in Supercritical CO_2-Ionic Liquid Systems, **The Journal of Supercritical Fluids**, (2018), *just accepted*.

Springer springer.com

http://www.springer.com/us/book/9784431553083

On Sale Now!



2015, XIV, 270 p. 163 illus., 118 illus. in color.

Printed book

Hardcover
ISBN 978-4-431-55308-3

- **99,99 € | £90.00**
- ***106,99 € (D) | 109,99 € (A) | CHF 133.50**

Y. **Tanaka**, M. **Norton**, Y.-Y. **Li** (Eds.)

Topical Themes in Energy and Resources

A Cross-Disciplinary Education and Training Program for Environmental Leaders

- Gives a comprehensive, birds-eye view of numerous issues in energy and resources
- Presents the work of leading researchers in a number of fields
- Provides a critical resource for those involved in cross-disciplinary and trans-disciplinary research programs and educational courses

Moving towards a more sustainable world requires a complete revolution in the way we manage energy and resources. However, from an academic perspective, this theme is so broad that most educators and researchers tend to focus on just one aspect, and maintaining the broad viewpoint which is necessary for making strategic judgments becomes difficult. Tohoku University addressed this challenge when developing a new education and training program for environmental leaders and brought together the extensive range of expertise available in specific fields into one special course which forms the basis of this book. Now in one volume, both students and educators can be brought up to date on a wide range of critical issues currently being addressed in the field of energy and resources. Issues covered include several critical ones in the energy field (low-energy technologies, renewable energies such as the hydrogen economy, and geothermal energy). Chapters on resources include availability (for instance, rare earth metals), extraction and recycling of metals and plastics, and technological solutions to specific waste-disposal problems. In addition, broader strategic issues such as limits to growth and the interaction between the economic system and environmental issues are addressed. Even though each chapter provides topical data and knowledge from disparate and specialized fields, the book is written at a level that is readily understandable by students from all scientific, engineering, and humanities fields.

6. Concluding remarks

* Carbon dioxide (CO_2) can be used to develop green chemical processes and new low energy technologies

* Replacement of hazardous solvents with safe solvent mixtures will lead to new technological developments

* Chemical processes that use CO_2 are essential for future sustainable development

More Information?

Homepage:

http://www.che.tohoku.ac.jp/~smith/index.html