Federal University of São Paulo.
Sea Institute IMAR

Session: *water handling*

PRODUCED WATER : SEPARATION, CHARACTERIZATION AND TREATMENT.

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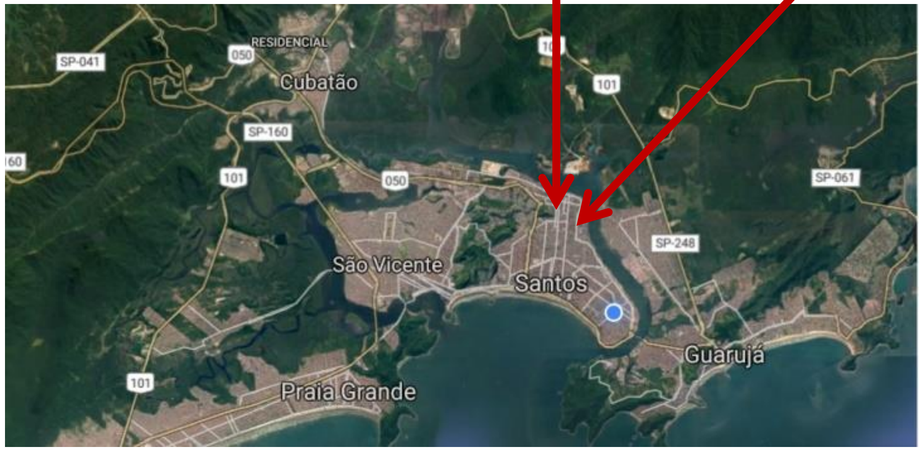
Petroleum Laboratory -**LabePetro**

SANTOS – STRATEGIC CITY IN THE OIL FIELD

Refinery in Cubatão

UNIFESP

USP



Santos → São Paulo (70 Km)

The scenario is favorable to develop research in petroleum and water handling

Federal University of São Paulo - UNIFESP

Sea Institute

Courses

- Environmental engineering
- Petroleum engineering
- Bachelor in science and technolog

Instituto do Mar
UNIFESP

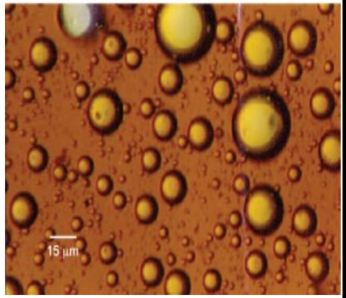
OPERACIONAL PROBLEM

√Unstable of asphaltenes

√ Paraffins

√ Incrustation

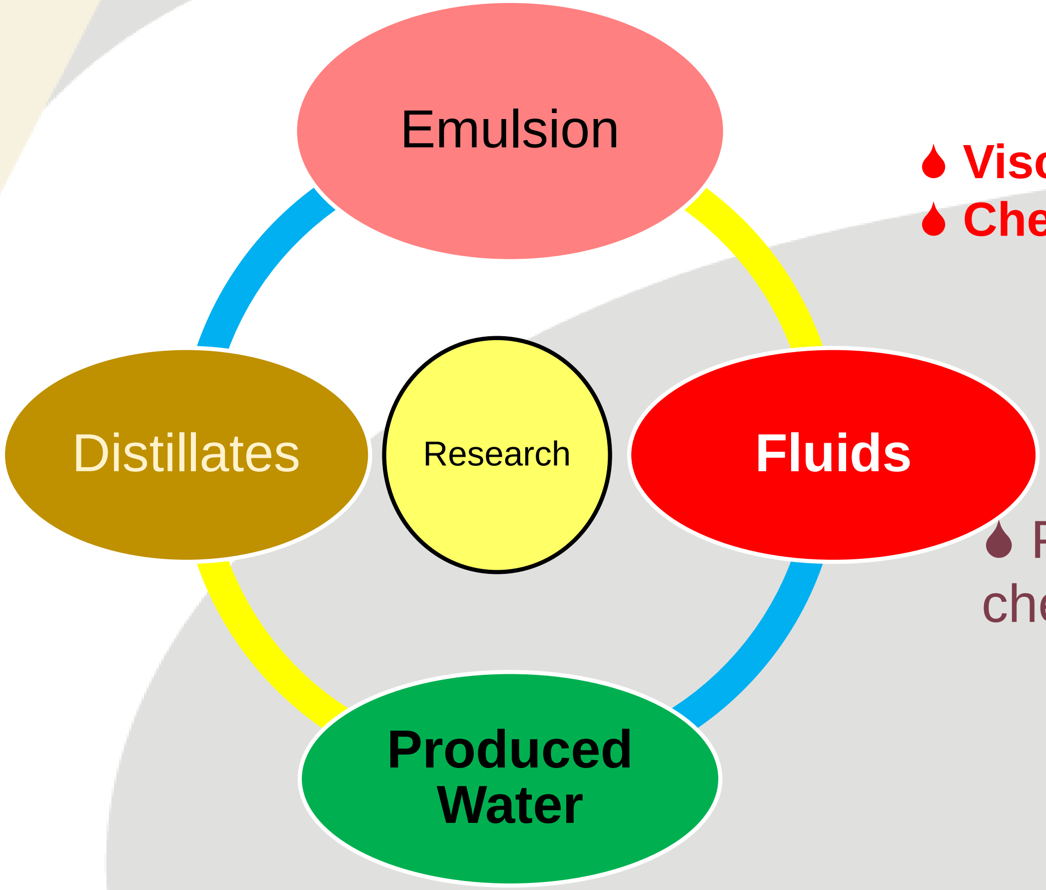
√Hydrate



√Water production

Research Group

- Droplet size distribution



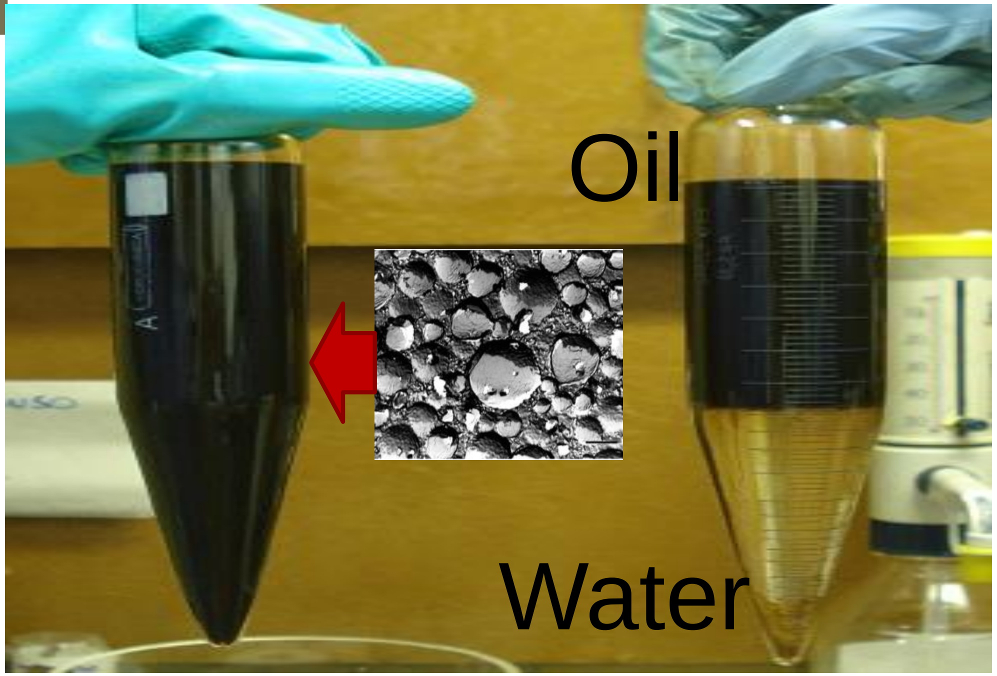
- **Viscosity model**
- **Chemical signature**

- Physical and chemical

Refinery water

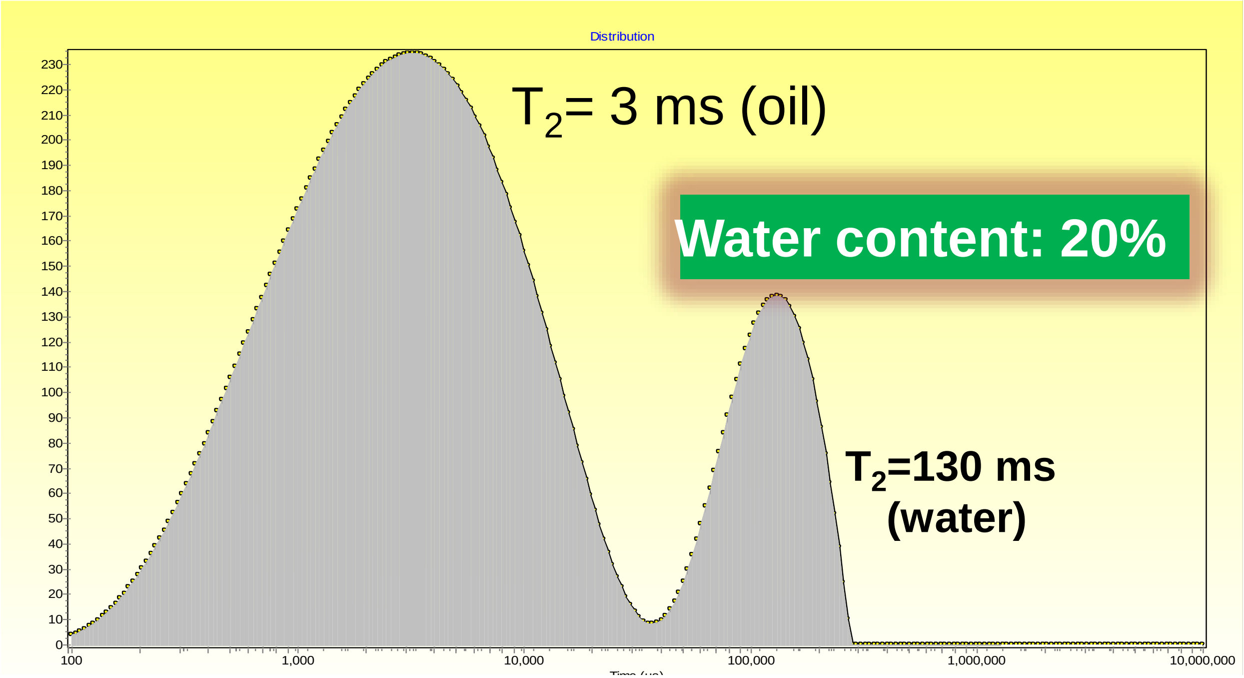
2. PETROLEUM EMULSION and SEPARATION PROCESS

Emulsions are dispersions of droplets of one liquid in another immiscible liquid.



Emulsions are undesirable

Quantification of the Water



T_2 distribution curve

- **Advantage-** **I**t is not need to perform any physical or chemical process to quantify water
- **Analysis time < 1min**

3. DETERMINATION WATER BY NMR

Water Content

Research Article

Magnetic Resonance in Chemistry

Received: 3 March 2011 Revised: 18 June 2011 Accepted: 9 August 2011 Published online in Wiley Online Library: 15 February 2012

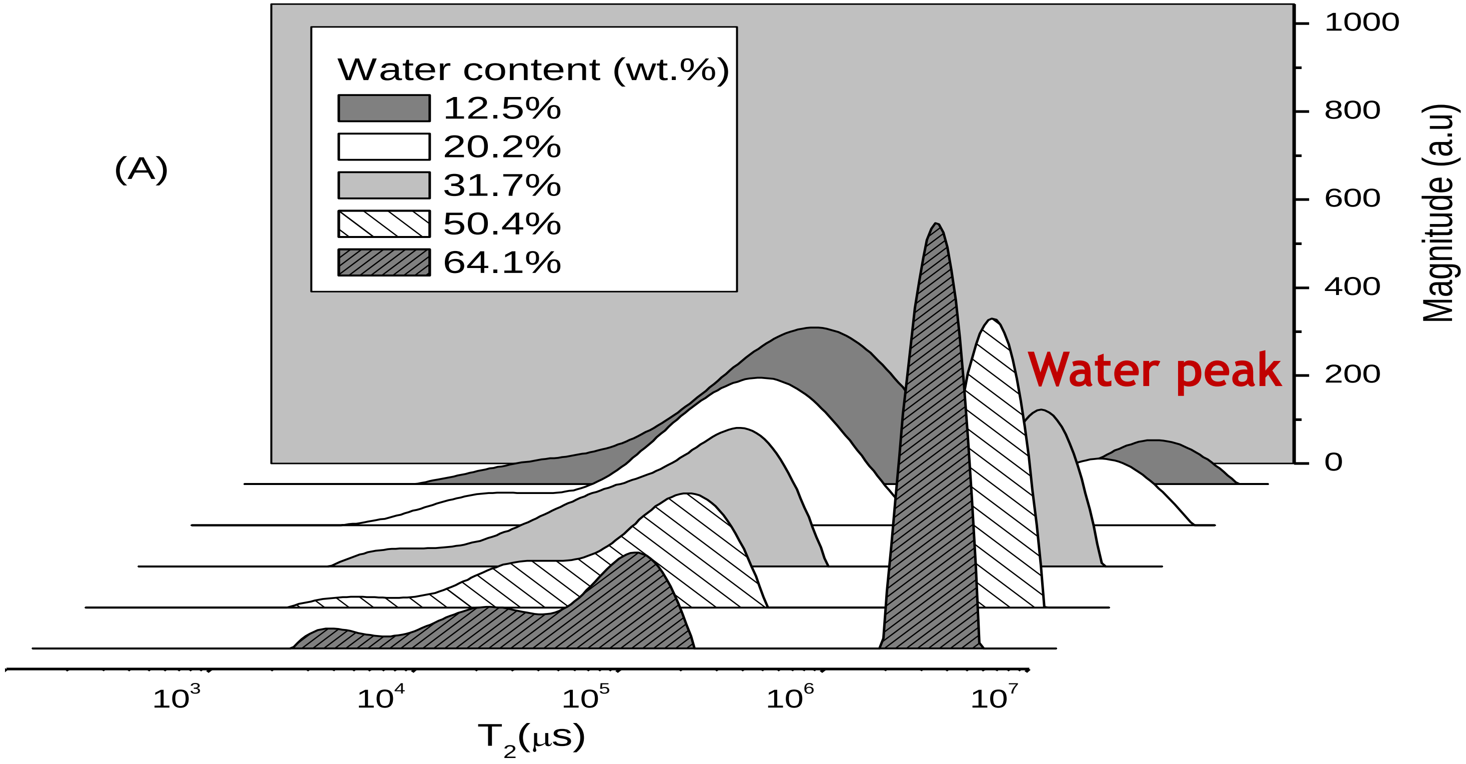
(wileyonlinelibrary.com) DOI 10.1002/mrc.2798

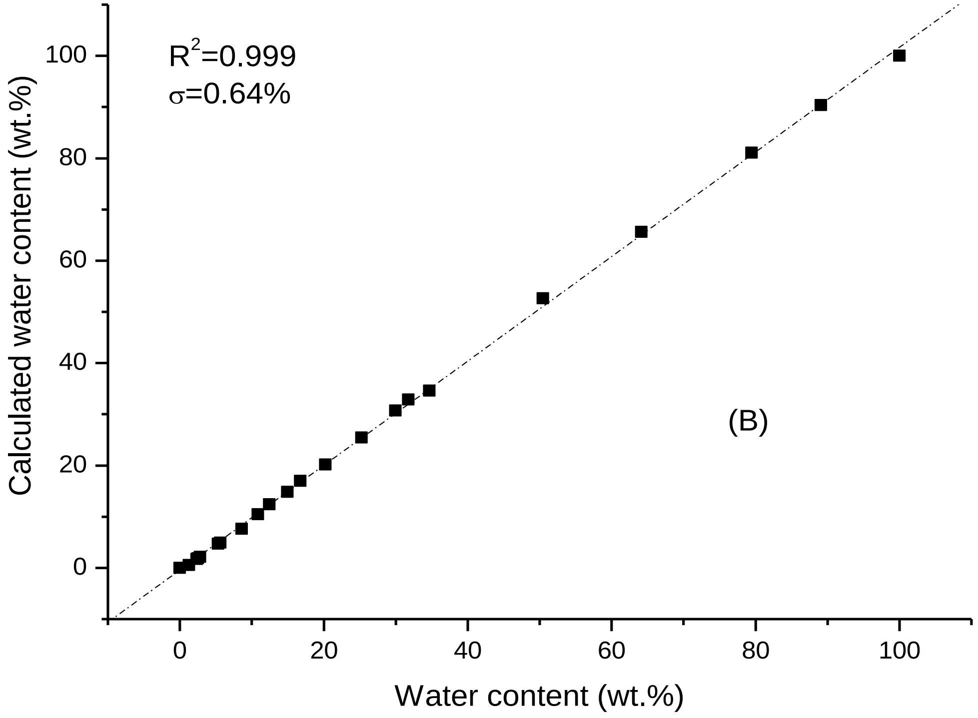
Studies on crude oil-water biphasic mixtures by low-field NMR

Renzo C. Silva,[a] Giovanna F. Carneiro,[a] Lúcio L. Barbosa,[a] Valdemar Lacerda Jr.,[a]* Jair C. C. Freitas[a,b] and Eustáquio V. R. de Castro[a]

Low-field ^{1}H NMR was used in this work for the analysis of mixtures involving crude oils and water. CPMG experiments were performed to determine the transverse relaxation time (T_2) distribution curves, which were computed by the inverse Laplace transform of the echo decay data. The instrument's ability of quantifying water and petroleum in biphasic mixtures following different methodologies was tested. For mixtures between deionized water and petroleum, one achieved excellent results, with root mean squared error of cross-validation (RMSECV) of 0.8% for a regression between the water content (wt %) and the relative area of the water peak in the T_2 distribution curve, or a standard deviation of 0.9% for the relationship between the water content and the relative water peak area, corrected by the relative hydrogen index of the crude. In the case of biphasic mixtures of Mn^{2+}-doped water and crude oils, the best result of RMSECV = 1.6% was achieved by using the raw magnetization decay data for a partial least squares regression. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: low-field NMR; petroleum; crude oil; biphasic mixtures





Magn. Reson. Chem. **2012**, *50*, 85–88

4. Water Content

Fuel 176 (2016) 146–152

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

ELSEVIER

Application of low field NMR as an alternative technique to quantification of total acid number and sulphur content in petroleum from Brazilian reservoirs

Lúcio L. Barbosa [a,*], Cristina M.S. Sad [b], Vinícius G. Morgan [b], Paulo R. Figueiras [b], Eustáquio R.V. Castro [b]

Oil	Field	Water content (% v/v)	API gravity	Type
1	A	0.9	28.7	Medium
2	A	1.0	28.2	Medium
3	A	1.2	28	Medium
4	A	0.9	27.5	Medium
5	B	1.2	20	Heavy
6	B	1.1	19.8	Heavy
7	A	1.8	27.4	Medium
8	A	1.1	28.2	Medium
9	A	1.2	28.3	Medium
10	C	0.1	16.8	Heavy
11	C	0.2	16.9	Heavy
12	A	1.6	28.4	Medium
13	A	1.5	28.7	Medium
14	A	1.4	28.5	Medium
15	A	1.2	28.9	Medium
16	A	1.4	28	Medium
17	A	1.0	27.9	Medium
18	A	1.4	28.6	Medium
19	A	1.3	28.5	Medium
20	A	1.7	28	Medium
21	B	0.5	19.6	Heavy
22	B	0.4	19.5	Heavy
23	A	1.9	28	Medium
24	C	0.2	17.1	Heavy
25	C	0.1	17.2	Heavy
26	A	1.4	28.2	Medium
27	B	0.5	20.2	Heavy
28	B	0.4	20.1	Heavy
29	B	0.6	20.3	Heavy
30	B	0.5	20.1	Heavy

4. Determination of the Water Content by ASTM Method Method

96 Global Journal of Energy Technology Research Updates, 2014, 1, 96-103

Relaxometric Study Concerning the Action of A Complexant Agent on Petroleum

Flávio Vinicius Crizóstomo Kock, Elói Alves Silva Filho, Eustáquio Vinícius Ribeiro de Castro, Valdemar Lacerda Jr and Lúcio Leonel Barbosa*

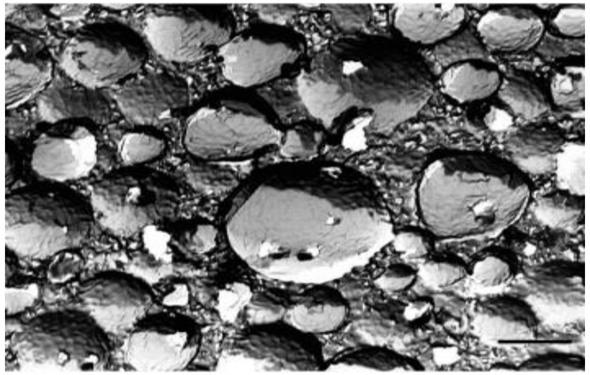
Why BSW is important to water handling?

Table 1: Physical Properties of Petroleum Used in the Research

Petroleum	°API	Viscosity ($mm^2 s^{-1}$)	Density ($g cm^{-3}$)	BSW (v/v)
1	20.1	553.63	0.9330	9.00
2	19.7	651.82	0.9355	36.00
3	17.0	673.93	0.9530	12.00
4	18.2	2131.40	0.9450	12.00
5	20.0	528.01	0.9342	26.32
6	19.6	671.12	0.9363	10.00
7	19.7	581.50	0.9357	8.00
8	22.9	58.11	0.9164	0.20

Refinery: BSW <1%

4. Influence of Water Content on the



A/O Emulsion

♦ Viscosity Model in Emulsions

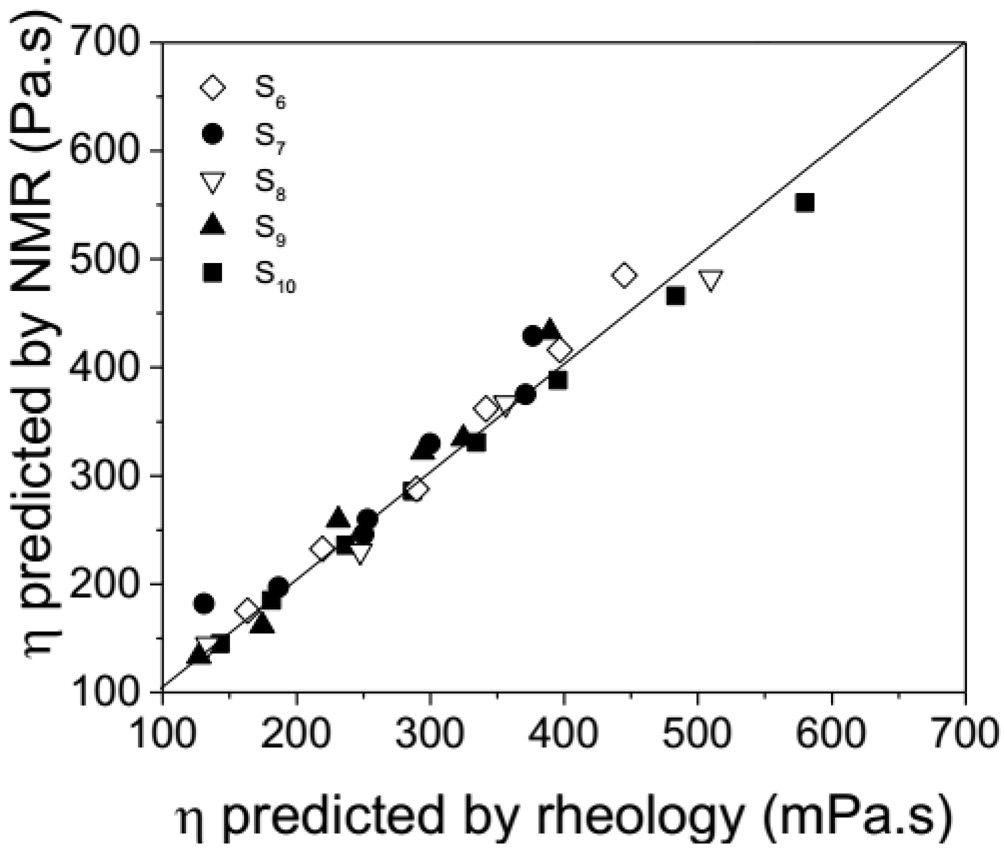
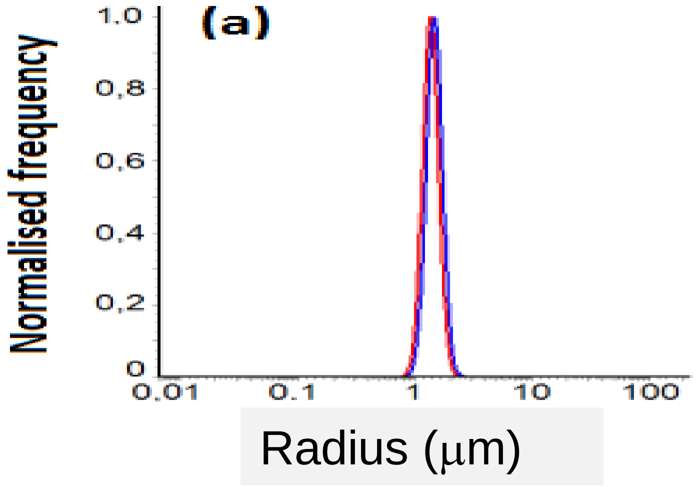


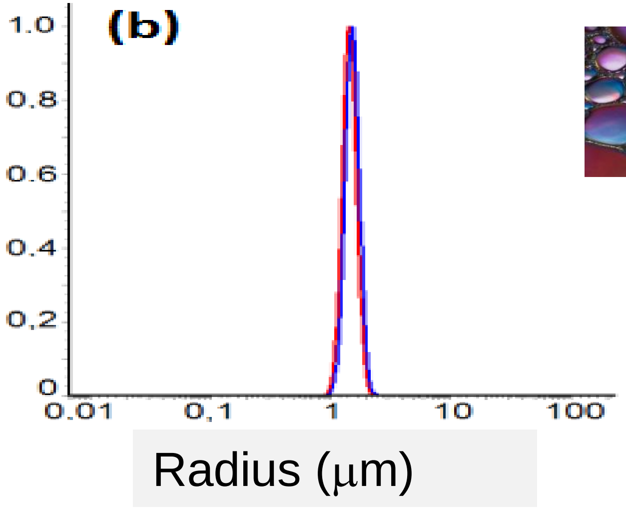
Table 5: Physical and chemical property of five crude oil used to validation.

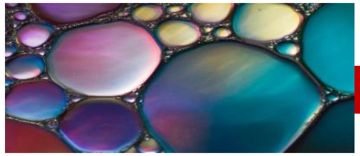
Property	S_6	S_7	S_8	S_9	S_{10}	*ASTM*
Water Content (%v/v)	0.30	0.50	0.50	0.05	0.50	D4377
Density at 20ºC (gcm^{-3})	0.9199	0.9192	0.9185	0.9167	0.9164	D5002
API gravity	21.7	21.8	21.9	22.2	22.3	D1250
TAN (mg $KOHg^{-1}$)	1.49	1.37	1.44	1.41	1.22	D664
Viscosity a 40ºC (mPa.s)	69.6	67.4	65.6	59.7	58.4	D7042
STI NaCl ($mgkg^{-1}$ NaCl)	441	643	624	76	661	D6470

•T. Amorin, Lúcio L. Barbosa, Rheological study of W/O oil emulsion by low-field. Submmited to Petroleum Science and Engineering, **2017.**

5. Droplet Size Distribution - DSD







Emulsion	R_{00} (μm)	Std (u.a)	Disperse phase (%m/m)	V (rpm)	t (min)
AM 18	1.380	0.147	29.17	3000	3
AM 22	1.681	0.096	21.40	3000	3
AM 24	1.750	0.179	5.03	3000	3
AM 25	1.640	0.202	3.34	3000	3
AM 26	1.661	0.130	1.51	3000	3

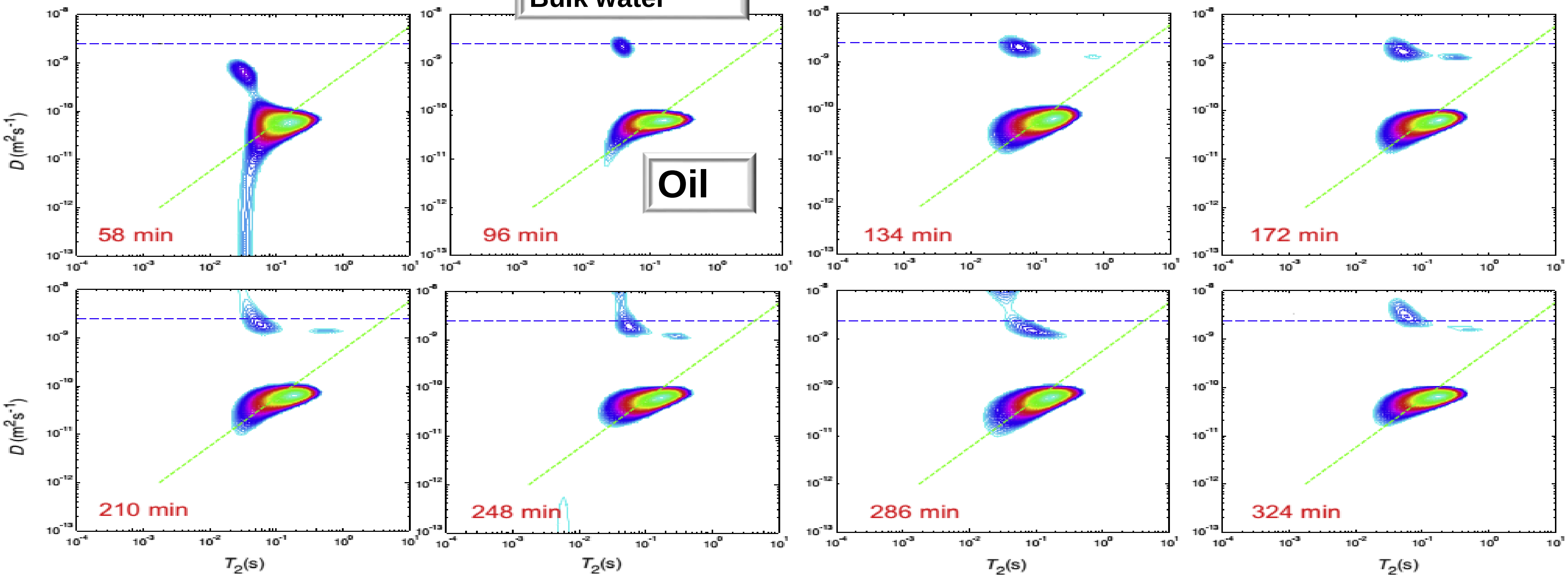
The DSD affects:
rheological properties, viscosity, flow, stability and treatment method

- **First work in Brazil using NMR**
- **Winner of the award of Brazilian Society of Nuclear Resonance**

Morgan, V.G; Barbosa, L. L. ; Sad, C.M.; Vasconcellos R. B. Castro, E. V. R, Lacerda Jr, V. Subm to Energy&Fuel, 2017

6. Dynamic of the Desemulsification Process

With desemulsifier: 96min



D–T2 plot **Fig. 5.** D–T_2 plots obtained in eight consecutives experiments to monitor the phase separation process for the emulsion with the addition of commercial demulsifier A.

Giovanna F. Carneiro, Renzo C. Silva, Lúcio L. Barbosa et al. Fuel 140 (2015) 762–769

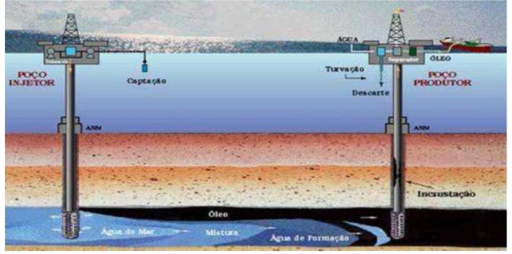
Current project

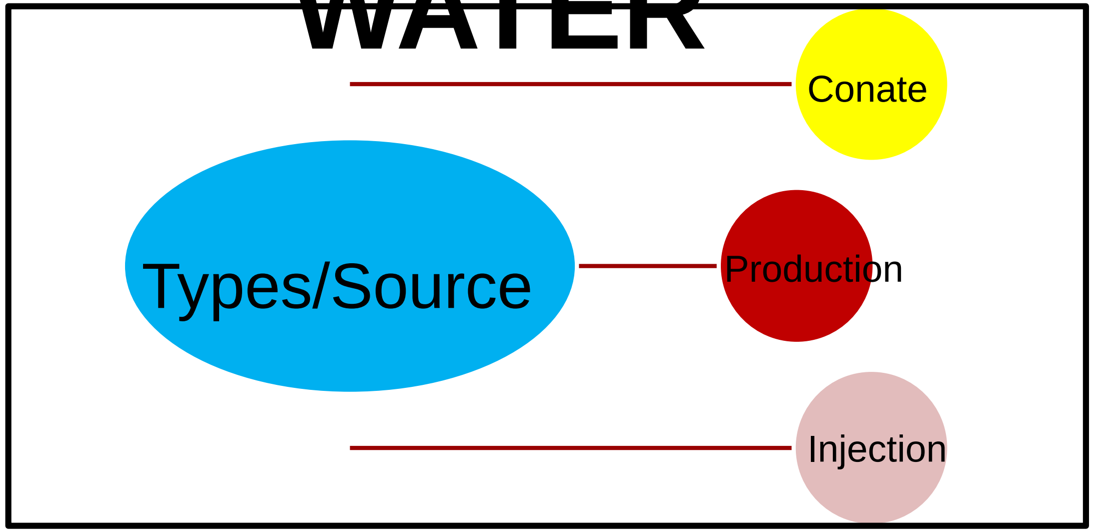
Title: Development of Methodologies for Determine the Properties of Brazilian Petroleum.
Objective: Quantify the water and sediment content, viscosity and other properties.

Funding: FAPESP (process Nº: 2017/02856-0).
Coordenation: Lúcio L. barbosa

10. Produced Water

PRODUCED WATER





Problem; Incrustation

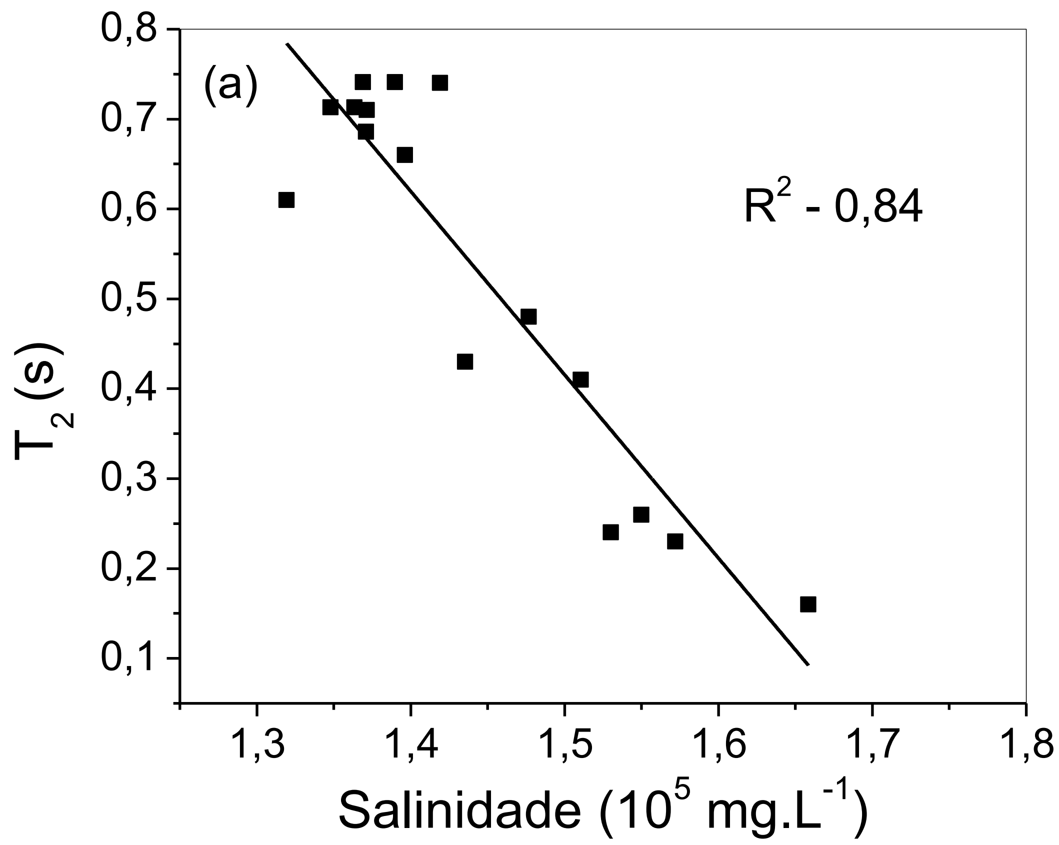
$BaSO_4$, $CaSO_4$, $SrSO_4$ e $CaCO_3$

Estações	pH	NaCl	HCO_3	SO^{2-}_4	Ca^{2+}	Mg^{2+}	Ba^{2+}	Fe^{2+}	Solid
1	6,9	53000	200	18	3400	1070	80	11	228
2	6,7	45000	236	362	5100	1580	42	10	185
3	6,9	75000	160	51	5200	1270	150	10	265
4	6,7	76000	173	250	4900	1600	10	12	314
5	7,3	45000	243	**1160**	2900	1230	0	1	11

PRODUCED WATER - *OFFSHORE*

Nuclear Resonance Magnetic – An New Technology.

Salinity



$$T_2 = (-2{,}04 \pm 0{,}23) + (3{,}48 \pm 0{,}34) * Salinidade(mg.L^{-1})$$

Work of the master's student - N. Pereira

PRODUCED WATER

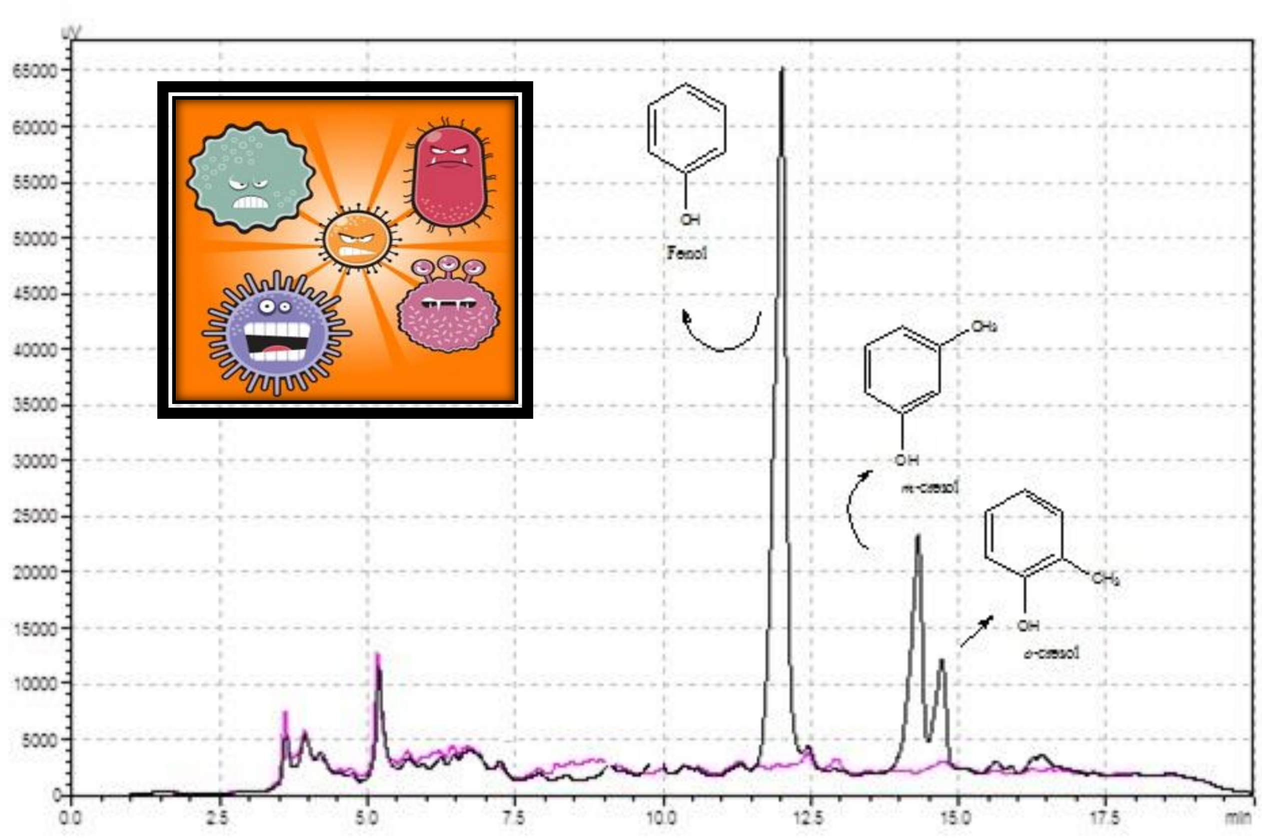
Quantification by Spectrometry (ICP OES)

	Concentration (µg.kg^{-1})						T_2
	Cr	Co	Fe	Mn	Ni	Cu	
1	0,75	6.35	88.96	258.01	14.10	< LD	0.74
2	< LD	6.63	61.03	1182.32	13.69	< LD	0.25
3	2.18	6.79	9.92	220.29	12.40	< LD	0.74
4	2,52	7.26	122.37	714.79	11.14	< LD	0.32
5	1.03	6.07	190.62	324.93	11.76	< LD	0.71
6	2.13	5.88	472.56	295.75	12.25	< LD	0.68
7	27.42	5.19	163.25	384.83	33.83	< LD	0.74
8	189.02	9.65	756.77	391.19	146.80	11,63	0.71
9	6.79	5.53	84.81	774.52	17.96	< LD	0.46
10	< LD	6.48	326.46	376.46	12.17	< LD	1.09
11	2.22	7.42	4.61	224.25	19.76	< LD	1.05
12	1.91	6.52	8.63	309.48	12.28	< LD	0.77

knowing a produced water's constituents, producers can determine the proper application of scale inhibitors

Biodegradation of oil refinery wastewater

Bioremediation is defined as the use of bacteria, fungi or plants to break down or degrade toxic chemical compounds accumulated in the environment at excess levels to bring them to normal levels (considered acceptable).

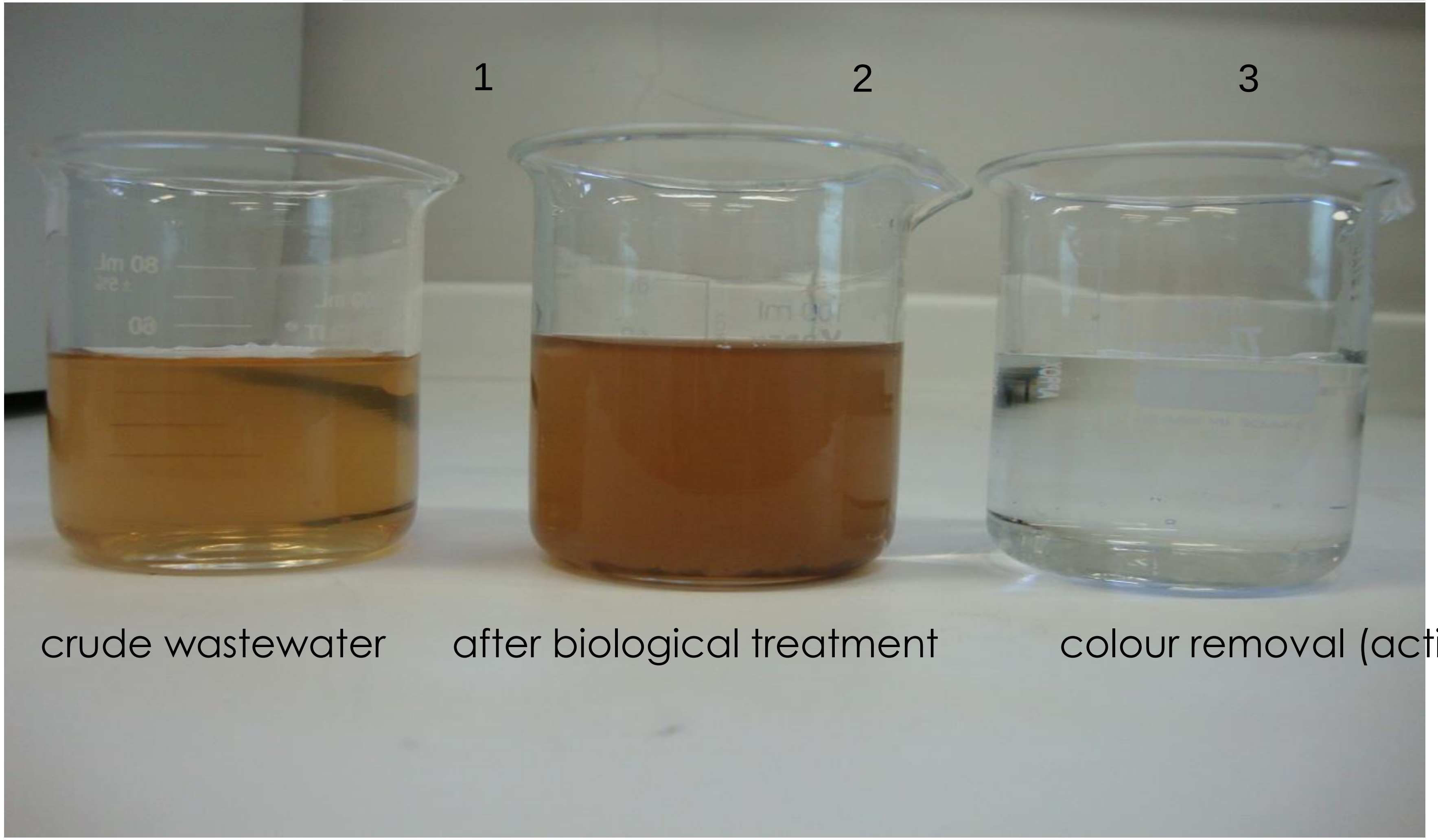


HPLC Profile

Advantage:
Low cost, 60-90% less than other technologies

In black: phenols, *orto* and *meta* cresol (crude wastewater)
In pink: treated wastewater (total removal of contaminants)-after 48 h

Biodegradation of phenolic wastewater



Reuse in cooling system

Profa. Elen Aquino

Challenges

From a single colony on plate to....

Bench top scale....(optimized conditions)

Profa. Elen Aquino

Advanced Oxidation Processes (AOP)

Objective: Use of the Heterogeneous photocatalysis to remove organic pollutant present in water by UV or Visible radiation (white-light), and semiconductor based catalysts (eg. Magnetite, niobium oxide, clays..).

Advantages:

✓ Treatment of water containing organic pollutant.
✓ Degradation of these organic pollutant to CO_2 and H_2O.
✓ This application can be extended to the treatment of **"produced water"** in offshore platforms.

Funding:
✓The São Paulo Research Foundation (FAPESP) (process Nº: 2014/24940-5).

Hydrogen Production by Water splitting (or photo-reforming).

Objective: Producing hydrogen by photocatalytic fractionation of water containing organic pollutant (eg, methanol or higher alcohols, or octane as Sacrificial agent) using Pt-based catalysts and UV or Visible (white light) radiation.

Advantages:

✓Treatment of water containing organic matter (this process can be extended to the treatment of **"produced water"** in offshore platforms).

✓Production of high-valued product: "Hydrogen" as new source of energy.

✓Solution for two problems: a energetic problem and an environmental problem.

Funding:

✓The São Paulo Research Foundation (FAPESP) (process Nº: 2014/24940-5).

Final Considerations

- The water produced affect the pumping system and increase the cost of the production

- Separation and Quantification are important to water handling

- It is essencial:
  - Reduce the water produced and the water inflow
  - Develop new technology to reuse of water production

- The produced water's characteristics can help increase production

Acknowledgement

UNIFESP
UNIVERSIDADE FEDERAL DE SÃO PAULO
1933

Instituto do Mar
UNIFESP

FAPESP
FUNDAÇÃO DE AMPARO À PESQUISA DO ESTADO DE SÃO PAULO

Thank you for the attencion!

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