INVESTIGATION OF THE EFFECT OF HYDRODYNAMICS ON THE PRODUCTION OF PICKERING EMULSIONS IN BAFFLED STIRRED TANKS

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ABSTRACT

INVESTIGATION OF THE EFFECT OF HYDRODYNAMICS ON THE PRODUCTION OF PICKERING EMULSIONS IN BAFFLED STIRRED TANKS

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Pickering emulsions are emulsions stabilized by solid particles and are potential industrial scale alternatives to surfactant-based emulsions. The stability of Pickering emulsions depends on two factors: the physicochemical nature of the liquid-particle interface and the hydrodynamic conditions of the production process. Studies have been carried out on the physicochemical nature of the emulsions. This study investigates the effect of hydrodynamics on the production of Pickering emulsions in baffled stirred tanks. Silicon oil was dispersed into distilled water and stabilized with hydrophilic glass beads to form oil in water Pickering emulsions. The experiments were performed in a baffled 1 liter beaker. Two impellers were used at two different sizes to generate different flow patterns: the Rushton turbine (RT) for radial flow pattern and the Pitched Blade Turbine (PBT) for mixed flow pattern. The resulting droplet size distribution was then determined with a Malvern Mastersizer. The effects of hydrodynamic parameters such as the power per unit mass, Reynolds number, tip speed and Weber number on the droplet sizes were studied. For impellers with adequate flow, increasing the impeller speed decreased the droplet size of the emulsion. Decreasing the speed increased the droplet size of the emulsion. A speed hysteresis was observed in the emulsion formation. The energy
dissipated around the impeller zone and the size of the impeller high shear zone were found to be critical to the droplet size distributions of the emulsions. The breakup mechanism of the Rushton turbine was also found to be more favorable for the emulsion production.

Keywords: Pickering emulsions, Droplet coalescence, Stirred tank, Droplet size, Emulsification
ÖZ

PICKERING EMÜLSİYONLARI ÜRETİMİ İÇİN ENGELLİ KARIŞTIRMALI TANKLARDA HİDRODİNAMİĞİN ETKİSİNİN İNCELENMESİ

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Anahtar Kelimeler: Pickering emülsiyonu, Damlacık birleşimi, Karıştırma tank, Damlacık boyutu, Emülsifikasyon
For Mummy and Daddy
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LIST OF ABBREVIATIONS

ABBREVIATIONS

Roman characters

\( a_v \) - interfacial area per unit volume of the dispersed phase
\( d \) - Droplet diameter (m)
\( D \) - Impeller diameter (m)
\( d_{32} \) - Sauter mean diameter (\( \mu \)m)
\( d_{43} \) - Volume averaged diameter (\( \mu \)m)
\( d_{50} \) - Number mean diameter (\( \mu \)m)
\( kT \) - Thermal energy
\( N \) - Rotational Speed (rpm)
\( N_p \) - Impeller power number
\( N_E \) - Air entrainment speed (rpm)
\( N_{JD} \) - Just dispersed speed (rpm)
\( o/w \) - Oil in water
\( p_L \) - Laplace pressure
\( PBT \) - Pitched Blade Turbine
\( ppm \) - Power per mass (W/Kg)
\( R \) - Particle radius (\( \mu \)m)
\( R_1 \) - Droplet radius (\( \mu \)m)
\( Re \) - Reynolds number
\( RT \) - Rushton Turbine
\( T \) - Tank diameter (m)
\( u \) - local flow velocity (m/s)
\( \bar{u} \) - Root mean square average velocity
\( \hat{u} \) - Time averaged velocity
V  - Dispersed phase volume fraction
v/v  - volume fraction
$V_{\text{swept}}$  - Impeller swept volume (m$^3$)
$V_{\text{tank}}$  - Tank volume (m$^3$)
$V_{\text{tip}}$  - Tip speed (m/min)
W  - Baffle width (m)
w/o  - Water in oil
w/w  - Weight Fraction
$W_{\text{e}}$  - Weber Number

**Greek characters**

θ  - Particle contact angle
γ  - Shear rate
$\gamma_{\text{o/w}}$  - Oil-water interfacial tension (mN/m)
ρ  - Emulsion density (Kg/m$^3$)
ν  - Kinematic viscosity (cSt)
μ  - Emulsion viscosity (cSt)
$\mu_{\text{c}}$  - Continuous phase viscosity (cSt)
CHAPTER 1

INTRODUCTION

1.1. Emulsions

An emulsion is defined as two immiscible liquids in which drops of one phase (the dispersed phase) are encapsulated or enclosed within another phase (the continuous phase). Emulsions and emulsification processes are commonly encountered in many fields such as cosmetics, pharmaceutical, paints, food processing, oil and petrochemical industries. There are two basic types of emulsions. Oil-in-Water (O/W) emulsions and Water-in-Oil (W/O) emulsions. In O/W emulsions, the oil drops are dispersed and encapsulated within the water phase. In W/O emulsions, water is dispersed within the oil phase (Chen and Tao, 2005). For the formation of a stable emulsion, three conditions must be satisfied (Chen and Tao, 2005):

a) The two liquids must be immiscible or mutually insoluble in each other

b) Sufficient agitation must be applied to disperse one liquid into the other

c) An emulsifying agent must be present

The emulsifier plays an important role in the formation of emulsions. It lowers the interfacial energy between the phases. The emulsifier also adsorbs at the oil/water interface and prevents the coalescence of newly formed droplets due to electrostatic and steric repulsive forces. It stabilizes the emulsion and controls the type of emulsion to be formed. Conventionally, chemical surfactants or amphiphilic polymers are used to stabilize emulsions. However, there has been an increasing interest in the use of solid particles to produce highly stable emulsions.
1.2. Pickering Emulsions

Pioneering work by Pickering (1907) highlighted the possibility of solid particles adsorbing to an oil/water interface to form emulsions. Such emulsions are hence named Pickering emulsions. Binks (2002) further highlighted that particles could produce even more stable emulsions than surfactants. Pickering emulsions are also potentially less costly and more environmentally friendly alternatives to surfactant-based emulsions.

Binks et al. (2000, 2001, 2002), Aveyard et al. (2003), Tsabet and Fradette (2015), Arditty et al. (2003), and Madivala et al. (2009) highlighted critical properties of Pickering emulsions stabilized by different types of particles. Most of these studies attributed the formation of Pickering emulsions to the formation of a steric barrier around the dispersed phase droplets. The particle barrier network formation is summarized in three steps: 1) Approach of the particles to the interface 2) Adsorption and entrapment of the particles at the interface 3) Particle network formation and stabilization of the emulsion droplet by the adsorbed particles (Tsabet and Fradette, 2015).

Figure 1 illustrates how the wetting properties of the particles i.e. the particle contact angle (θ) is critical to the type and stability of emulsion droplets formed. For contact angles (θ) greater than 90°, the particles are hydrophilic and a larger portion of the particle stays in the water phase. It then forms an oil-in-water (o/w) emulsion. Contact angles less than 90° indicate hydrophobic particles. The particle resides more in the oil phase and form water-in-oil (w/o) emulsions. However, in extreme contact angles, the particles overly disperse in their preferred phase and stable emulsions are not formed. Contact angles close to 90° result in more stable droplets (Kaptay, 2006). Pickering emulsions also obey the Bancroft rule and the contact angle behavior only occurs when the dispersed phase volume fraction is smaller than or equal to that of the continuous phase and when the particles are initially dispersed in the phase with which they have the most affinity.
The highly stable nature and adsorption strength of Pickering emulsions can be explained thermodynamically by the detachment energy for the particle at the surface (Binks et al., 2000).

\[
\Delta E = \pi R^2 \gamma_{o/w} \left(1 + \cos \theta \right)^2 \gg kT
\]

where \( \gamma_{o/w} \) is the oil/water interfacial tension and \( kT \) is the thermal energy. At contact angles close to 90\(^\circ\), the detachment energy is orders of magnitudes greater than the thermal energy (\( kT \)). As a result, the particles can be thought of as irreversibly adsorbed and unaffected by random diffusion away from the interface.

To understand the stability of emulsion droplets, the Laplace pressure concept should be understood. The Laplace pressure (\( p_L \)) is the difference between the pressure inside and outside the droplet. It is given by the following equation:

\[
p_L = \gamma_{o/w} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
\]

where \( R_1 \) and \( R_2 \) are the radii of the curvature of the drop. For a spherical drop \( R_1 = R_2 = \frac{d}{2} \), where \( d \) is the diameter. The Laplace pressure increases when a large droplet deforms and breaks into smaller ones and the Laplace pressure of newly
formed smaller droplets is higher than that of the larger droplet. The smaller the droplet, the higher the Laplace pressure, hence more vigorous agitation (more energy) is required to transmit the necessary stress to break the droplet (Walstra, 1993). This indicates that the smaller the droplets, the more stable the emulsion.

1.2.1. Applications of Emulsions and Pickering Emulsions

Emulsions are important for various industries. Emulsion products include foods, drugs, paint, personal care creams and cosmetics. In food application, a range of food-grade particles such as fat crystals, proteins, starch nanocrystals and protein-polysaccharide complexes have been investigated and utilized in emulsion stabilization (Tang et al., 2005). Pickering emulsions can also be useful as delivery systems for functional foods as they can encapsulate several micro ingredients, offer protection against chemical degradation and possibly facilitate controlled delivery (Guzey and Mclements, 2012). Pickering emulsions with solid particles such as chitosan, clays and cyclodextrin have also been explored for pharmaceutical applications. The products with these particles are more suitable for in vivo use due to their biodegradability. They can also be applied for effective drug delivery. Emulsions are most commonly used in the cosmetics industry to formulate products such as sunscreen, lotions, nail polish and other products applied through the skin surface. Particles can be used in these formulations to provide longer storage capacities and less chance of reaction with the skin.

Dispersing an oil phase within an aqueous phase with solid particles can also be applied in the transport of heavy oils through pipelines. Since the oils are dispersed in a continuous phase of lower viscosity, the apparent viscosity of the mixture is decreased and therefore lower power is required to transport them. The oils can then be easily separated from the aqueous phase and the particle by exerting an external stimuli. This application can be made to the oil industry (Tang et al., 2005).
Several other applications of Pickering emulsions were reviewed by Yang et al. (2017). All the applications point to the fact that using solid particles to stabilize emulsions improve the product performance and enhance the product’s functions.

1.2.2. Physicochemical Properties of Pickering Emulsions

In producing Pickering emulsions, the size and stability of the emulsion droplets depend largely on two factors. The physicochemical nature of the liquid-particle interface and the hydrodynamic conditions of the production process. The physicochemical properties define the coverage potential of the particle and its affinity to adsorb onto the interface (Tsabet and Fradette, 2015). Extensive research has been done on the effect of the physicochemical properties of the particles on the stability of Pickering emulsions. Different types of particles such as silica, metal oxides, clay, carbon, proteins, polymers and many more can be used to produce Pickering emulsions with varying characteristics (Aveyard et al., 2003). Smaller particles have been found to form smaller droplets and form more stable emulsions (Binks and Lumsdon, 2001). Binks and Lumsdon (2001) also showed that increasing the concentration of particles decreases the size of the droplet formed. With regards to particle shape, spherical shaped particles are seen to disperse well in the continuous phase and form stable droplets. However, ellipsoidal particles are seen to produce the most stable droplets (Madivala et al., 2009). Other properties such as aqueous phase pH, oil/particle affinity, oil polarity, and oil viscosity have been seen to have effects on the emulsion stability (Tsabet and Fradette, 2015). Some relevant research on the physicochemical properties of Pickering emulsions are presented in Table 1.

Table 1: Physicochemical properties of Pickering emulsions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Wettability</td>
<td>Yan et al. (2001), Aveyard et al. (2003), Binks et al. (2000, 2005)</td>
</tr>
<tr>
<td>Oil Polarity</td>
<td>Binks and Whitby (2005), Golemanov et al. (2006)</td>
</tr>
<tr>
<td>Parameter</td>
<td>Reference</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>Oil/Particle Affinity</td>
<td>Golemanov et al. (2006)</td>
</tr>
<tr>
<td>Particle Size</td>
<td>Binks and Lumsden (2001), Tarimala and Dai (2004)</td>
</tr>
<tr>
<td>Particle Concentration</td>
<td>Arditty et al. (2003)</td>
</tr>
<tr>
<td>Particle Size Distribution</td>
<td>Tarimala and Dai (2004)</td>
</tr>
<tr>
<td>Oil Viscosity</td>
<td>Golemanov et al. (2006), Tsabet and Fradette (2015)</td>
</tr>
<tr>
<td>Particle Shape</td>
<td>Madivala et al. (2009)</td>
</tr>
<tr>
<td>Aqueous Phase pH</td>
<td>Yan and Masliyah (1996)</td>
</tr>
</tbody>
</table>

### 1.3. Immiscible Liquid-Liquid Mixing

An immiscible liquid–liquid system is a system consisting of two or more mutually insoluble liquids present as separate phases: a dispersed phase and a continuous phase. The dispersed phase is usually smaller in volume than the continuous phase. Liquid-liquid mixing is important in various processes such as polymerization, solvent extraction, and emulsification and can be applied in chemical, pharmaceutical, petroleum and food production fields. Immiscible liquid mixing typically involves either an oil-in-water (O/W) or a water-in-oil (W/O) process (Leng and Calabrese, 2004). The most common purposes for such dispersions are to form either a stable emulsion or a dispersion for mass transfer, which can be separated later. The dispersed phase disperses into droplets within the continuous phase. Controlling the average droplet size and droplet size distribution is critical to emulsification. Emulsification processes depend on repeated droplet dispersion and coalescence. These phenomena control the final resulting droplet size.

### 1.3.1. Droplet Breakup and Coalescence

Droplet break-up and coalescence are the dominating processes that control the equilibrium emulsion droplet size. Figure 2 shows different steps that occur in emulsification. The figure shows the breakup of a large dispersed phase drop to
smaller drops. The dispersed phase drops are deformed by mechanical forces around it and the deformation of individual drops is resisted by surface and internal viscous forces (Zhou and Kresta, 1998). A balance of these forces determines if the drop will break or not. Drop break-up occurs when the mechanical forces exerted by the surrounding fluid exceeds the resistance forces. All fluid dynamical forces that cause drop break-up are commonly referred to as shear forces. Shear forces are mostly responsible for drop break-up but breakup also occurs as a result of collision with the vessel walls, baffles, impellers (Leng and Calabrese, 2004). The particles adsorb onto the newly formed drop interface. Some drops are partially covered by the particles and some are fully covered. The particles form a barrier and prevent fully covered drops from coalescing when they collide. However, when partially covered drops collide as shown in Figure 2, coalescence occurs. For coalescence to occur, droplets must collide and stay together for certain time. The drop coalescence is influenced by the droplet collision rate and the rate of adsorption of the emulsifier onto the surface of newly created droplets; the faster the adsorption of the emulsifier, the lower the chance of coalescence (Siddiqui and Norton, 2012). In order to obtain small stable emulsions, droplet breakup must be maximized and droplet coalescence must be minimized.

Figure 2: Droplet break-up and coalescence
Based on the dispersed phase concentration (V), liquid-liquid systems can be categorized as (Leng and Calabrese, 2004):

- **Dilute systems (V < 0.01):** The dispersion is affected only by hydrodynamics and coalescence is neglected because only a few collisions occur. This simplification makes it easier to model fundamental dispersions. Coalescence can become significant for systems at V ≥ 0.05. Numerous studies have been done to understand and correlate drop size distributions of liquid-liquid distributions in mixing equipment. (Wichterle, 1995; Calabrese et al., 1986; Coulaloglou and Tavlarides, 1976; Walstra, 1993; Zhou and Kresta, 1998).

- **Moderately concentrated systems (V < 0.2):** Coalescence is observed, but ideal dilute dispersion theories may still be applied and it is still possible to predict the drop size distribution.

- **More concentrated systems (V > 0.2):** Coalescence is dominant. Coalescence and dispersion occur simultaneously in different regions of the vessel. This behavior is difficult to model but such systems are more common in industry. The drop size distribution for such systems depend on a number of factors such as the completeness of the dispersion process, the local turbulent intensities as a result of impeller selection, vessel design, vessel size and operating conditions. In this paper, a concentrated and coalescing system is studied.

### 1.3.2. Droplet Size Distribution

The droplets formed from emulsification vary in size and exist in a continuous size spectrum. The droplet size of the emulsion is represented in terms of a droplet size distribution. The droplet size distribution is commonly unimodal. However, they can also be bimodal or even trimodal. Multimodal distributions occur as a result of multiple and unusual breakage patterns. Excessive coalescence pattern and
emulsifier agglomeration can also lead to bimodal distribution. The droplet size
distribution can be represented by several mean values (Leng and Calabrese, 2004):

1) $d_{32}$ (Sauter mean diameter)

$$d_{32} = \frac{\sum_{i=1}^{m} n_i d_i^3}{\sum_{i=1}^{m} n_i d_i^2}$$  \hspace{1cm} (3)

This diameter is formed from the ratio of the third to second moments of the drop
size distribution. $m$ is the number of size classes describing the distribution. $n_i$ and $d_i$
are the number of drops and nominal diameter of drops in class $i$ respectively. This
diameter is related to the surface area of the drops. It is the common diameter of
choice as it is directly related to the volume fraction of the dispersed phase ($V$) and
the interfacial area per unit volume of the dispersed phase ($a_v$):

$$d_{32} = \frac{6V}{a_v}$$  \hspace{1cm} (4)

2) $d_{43}$ (Mass averaged diameter)

This is another used mean drop diameter. It is the ratio of the fourth to third
moments of the distribution and represents a mass-weighted average.

$$d_{43} = \frac{\sum_{i=1}^{m} n_i d_i^4}{\sum_{i=1}^{m} n_i d_i^3}$$  \hspace{1cm} (5)

This diameter is used in this paper since it is not significantly affected by the
presence of excess particles in the system.

3) $d_{50}$, $d_{10}$, $d_{90}$

These are number means expressed in terms of cumulative volume frequency. It
represents the first to zero moments of the distribution.
\[ d_n = \frac{\sum_{i=1}^{i=m} n_i d_i}{\sum_{i=1}^{i=m} n_i} \]  

(6)

d_{50} is the size at which 50% by volume of all drops are smaller than. \( d_{10} \) the size for 10%, and \( d_{90} \) the size for 90%.

### 1.3.3. Mixing Equipment

The mechanical agitation required to produce emulsions can be provided by several mixing equipment. The selection of the equipment is dependent of the desired process result and desired droplet size distribution. For example, as a rule of thumb (Mitkowski and Szaferksi, 2012):

- For \( d_{32} > 300 \ \mu m \): Stirred tanks without baffles but equipped with a special type of impeller can be used
- For \( 30 \ \mu m < d_{32} < 300 \ \mu m \): Stirred tanks with baffles can be used.
- For fine dispersions (0.1 \( \mu m < d_{32} < 50 \ \mu m \)): Rotor stator mixers, impingement mixers, colloid mills homogenizers (Leng and Calabrese, 2004) or ultrasonic mixers (Droog, 2012) can be used.
- For dispersions in a process line: Static pipeline mixers are used.

Wibowo et al. (2001) split emulsion mixing equipment into two categories depending on their process structure: pre-emulsification and homogenization equipment. Pipeline mixers, and stirred tanks fall under the pre-emulsification equipment as they yield coarse emulsions with relatively larger droplet sizes. Colloid mills, homogenizers, ultrasonic mixers and rotor stators fall under homogenization equipment as they yield fine emulsions. Wibowo et al. (2001) compiled a few rules of thumb to consider when selecting equipment for emulsification processes.
1) If the emulsion is sensitive to temperature change, select an equipment without dead or stagnant zones such as a fully mixed stirred tank with a scraper.

2) If the viscosity ratio between the dispersed and continuous phase is greater than 4, an equipment in which break-up occurs solely in a shear flow, such as a colloid mill, should not be used.

3) If the continuous phase viscosity is greater than 0.02 Pa s, do not use a pressure homogenizer.

4) To achieve a more uniform shear rate distribution within the vessel, use an impeller with high impeller to vessel diameter ratio.

5) To minimize air entrance into the system, completely submerge the impellers.

Table 2 presents a summary of equipment used in emulsification processes.

Table 2: Emulsification equipment (Adapted from Leng and Calabrese (2004))

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Desired result</th>
<th>Batch or continuous</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baffled stirred tank</td>
<td>30 µm &lt; d_{32} &lt;300 µm</td>
<td>Either</td>
<td>Generally used industrially. Agitation is provided by rotating impellers.</td>
</tr>
<tr>
<td>Unbaffled stirred tank</td>
<td>300 µm &lt;d_{32} &lt;1000 µm</td>
<td>Either</td>
<td>Generally used industrially. Agitation is provided by rotating impellers.</td>
</tr>
<tr>
<td>Static</td>
<td>10 µm &lt; d_{32} &lt;200 µm</td>
<td>Continuous</td>
<td>High-speed, high-</td>
</tr>
<tr>
<td>Mixer Type</td>
<td>Droplet Size</td>
<td>Mode</td>
<td>Description</td>
</tr>
<tr>
<td>----------------------------</td>
<td>--------------</td>
<td>---------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Pipeline mixer</td>
<td>1 µm &lt; d₃₂ &lt; 50 µm</td>
<td>Either</td>
<td>Dispersion is forced through gaps in the stator and circulated into the main body of the mix.</td>
</tr>
<tr>
<td>Rotor-stator mixer</td>
<td>1 µm &lt; d₃₂ &lt; 50 µm</td>
<td>Continuous</td>
<td>Droplets are broken by impingement onto a wall.</td>
</tr>
<tr>
<td>Impingement mixer</td>
<td>1 µm &lt; d₃₂ &lt; 50 µm</td>
<td>Continuous</td>
<td>Dispersion is forced through a thin valve and agitation is provided by the sudden pressure difference.</td>
</tr>
<tr>
<td>Pressure homogenizer</td>
<td>0.1 µm &lt; d₃₂ &lt; 10 µm</td>
<td>Continuous</td>
<td>Droplets are violently broken by cavitation in micro-turbulent flow.</td>
</tr>
<tr>
<td>Ultrasonic mixer</td>
<td>0.1 µm &lt; d₃₂ &lt; 10 µm</td>
<td>Batch</td>
<td>Continuous</td>
</tr>
</tbody>
</table>

### 1.3.4. Stirred Tank Mixing

A stirred tank vessel is generally a vertical cylindrical tank. The necessary agitation required for emulsification is provided by rotating impellers. The impellers pump the fluid around the tank and provide necessary shear for droplet break-up. Commonly used impellers include pitched blade turbines, propellers, paddles, hydrofoils and
disk turbines such as the Rushton turbine. Droplet dispersion in stirred tanks occurs mainly as a result of the shear provided in the impeller region. It could also be as a result of drops impinging on the tank wall (Hemrajani and Tatterson, 2004).

The resulting droplet size distribution can be influenced by adjusting some key process parameters. In stirred tanks, they are: the ratio of the liquid height (H) to the tank diameter (T), the ratio of the impeller diameter (D) to the tank diameter (T), the off-bottom clearance of the impeller, the impeller rotational speed, impeller flow pattern and the viscosity of the immiscible liquids.

Wall baffling has a significant influence on the flow behavior and resulting emulsion quality. Baffles are used in stirred tanks to prevent the formation of a vortex as shown in Figure 3. Without baffles, the flow created by impeller rotation is two dimensional and causes swirling action, i.e., solid body rotation. Wall baffles transform tangential flows to vertical flows, provide top-to-bottom mixing without swirl, and minimize air entrainment. (Hemrajani and Tatterson, 2004). For most vessels, the baffles are four vertical plates mounted at equal distances around the tank. Depending on the tank size and desired results, the baffle width is usually one-tenth or one-twelfth of the tank diameter (Dickey, 2015).

Figure 3: Baffled vs Unbaffled Tank
1.3.5. Impeller Types and Flow Patterns

The flow patterns in a stirred tank are important for the effectiveness of mixing. They are achieved by the impeller type and provide the motion to transport the tank volume from one region to another and provide adequate uniformity for the process.

Impeller selection is critical to producing liquid-liquid dispersions. The resulting drop size distribution can be influenced by the impeller flow patterns and shearing capacity. In this study, two impellers are considered. The pitched-blade turbine (PBT) and the Rushton turbine (RT).

The pitched blade turbines have four blades mounted around a hub at a 45º angle. Some pitched blade turbines may be mounted at 30 or 60º angles (Dickey, 2015). The PBT provide both axial and radial flow as a result of its inclined blade. The blades push the tank volume toward the bottom of the tank at an angle before the volume circulates back to the impeller. This is illustrated in Figure 4. PBTs are widely used for liquid blending and solid suspension. The PBT could be effective in suspending the droplets and particles in a Pickering emulsion system.

The Rushton turbine is characterized by 6 vertical blades mounted on a disc. It provides radial flow in the tank as shown in Figure 4. The impeller blades discharge the flow towards the tank wall where it recirculates back below and above the impeller. The RT also provides high shear around it. The RT is effective for gas and liquid-liquid dispersions.
1.3.6. Shear Distribution in Stirred Tanks

Data from a study by Mertzner et al. (1960) indicate the shear in a tank rapidly decreases with distance from the impeller blade tip. The maximum shear rate in the flow is proportional to the tip speed of the impeller ($\pi ND$). It occurs near the blade tip in high-speed jets and vortices. The average shear rate in the impeller region is $\gamma \sim KN$. Where $K$ is a proportionality constant that decreases rapidly with distance from the impeller blade tip. It varies between 5 and 40 for most impellers (Mertzner et al., 1960). The average shear rate in the entire tank is about one order of magnitude less than the average shear rate in the impeller region. The minimum shear can be found near the liquid surface and is about 25% of the average shear rate in the tank (Hemrajani et al., 2004).

Wernerrson et al. (1999) suggested that a stirred tank volume consists of two regions: a near-impeller region and a circulation region and that the turbulent energy dissipation near the impellers is more intensive than that in the circulation region by a factor of more than 100. Droplet breakup occurs predominantly in areas around the impeller because of the intense turbulence and high shear generated in this area (Hemrajani et al., 2004).
1.3.7. Significant Hydrodynamic Parameters for Immiscible Liquid-Liquid Mixing

The hydrodynamics of the system can be quantified and represented by parameters such as:

a) Tip speed ($V_{tip}$)

Turbulent flow is characterized by the presence of eddies, which means the local flow velocity, $u$, is different for the time average values, $\bar{u}$. Hence the root mean square average ($\bar{u}'$) is an important characteristic of turbulent flow. Turbulent flow consists of a spectrum of eddy sizes. The largest eddies have the highest $u'$. They then transfer their kinetic energy to smaller eddies with smaller $u'$. The small eddies in turn transfer their energy to even smaller eddies in a cascading form till it gets to the smallest eddy and dissipates the energy to heat. The smallest eddy size is known as the Kolmogorov scale. In fully turbulent flow, the flow field can be made dimensionless using a characteristic length scale and a characteristic velocity scale. The dimensionless velocities scale exactly with the characteristic velocity. In a stirred tank, this velocity is the tip speed of the impeller ($V_{tip} = \pi ND$). All velocities in the tank are proportional to the tip speed.

Constant tip speed is a commonly used scaling factor for stirred tanks. However, due to the complexities of drop coalescence and the influence of tank size on drop size distribution, using tip speed to scale up liquid-liquid dispersions might fail.

b) Power per mass

This is the average power entering through the shaft dissipated per unit mass in the tank ($P/\rho V_{tank}$). It is a representation of the local rate of dissipation of turbulent kinetic energy which in turn is a direct measure of local turbulence intensity. Since turbulence varies significantly over the tank volume, the power per unit mass in the impeller swept volume ($P/\rho V_{sweep}$) is accepted as a more accurate scaling variable (Machado et al., 2012). The advantage of using the swept volume is that it takes the
effect of impeller diameter into account for scale-up and comparison of impeller configurations. It is frequently used for scale-up and experimental design. In some studies, the equilibrium drop size of a liquid-liquid dispersion system can be correlated by confining the energy dissipation rate to the impeller swept volume (Zhou and Kresta, 1998). The power input into the tank is given in equation (3).

\[ P = N_p \rho N^3 D^5 \]  

Here, \( N_p \) is the characteristic power number of an impeller. The power per mass is an important parameter because it gives a representation of the energy dissipated by various impellers. The influence of the energy dissipated on the drop size distribution can then be observed.

c) Reynolds number

The Reynolds number (\( Re=ND^2/\nu \)) is a ratio of the inertial and viscous forces in a system. It is representative of the flow regime of a fluid flow system. For stirred tanks \( Re>20\ 000 \) indicates turbulent regime and \( Re<10 \) indicates laminar regime (Hemrajani et al., 2004). Values in between indicate transitional regime. At very high Reynolds numbers, inertial forces dominate and changes in viscosity have no effect on process results. The disturbances from the turbulent fluctuating velocities aids rapid dispersion and mixing. Machado et al. (2013) showed that although most literature state that an impeller \( Re>20\ 000 \) sustains turbulent flow, this rule is only valid for areas around the impeller. A substantial part of a bench scale tank away from the impeller is actually in transitional flow (Machado et al., 2013). Therefore, the Reynolds number can fail as a scaling factor because of a potential lack of turbulent flow in areas far from the impeller. However, at high \( Re \) equal Reynolds number among different geometries can give a direct comparison between impellers in terms of flow regime.

d) Weber number

A tank Weber number \( (We=\rho N^2D^3/\gamma) \) is the ratio of inertial (disruptive) to surface (cohesive) forces. The Weber number is a representation of the capacity of the
system to break drops. At a high Weber number, the disruptive forces are dominant and drop breakup is encouraged. This parameter has been used to model and scale droplet break-up in mixing systems.

1.3.8. Pickering Emulsion Production in Stirred Tanks

In the case of Pickering emulsions, the physicochemical and hydrodynamic factors come together to form the final drop size distribution. The particles adsorb onto the generated interface and a ‘limited coalescence phenomenon’ described by Arditty et al. (1994) occurs. The phenomenon assumes that the droplets formed will coalesce until they reach a coverage limit specified by the coverage potential and the interface generated. The determination of the final droplet size depends on the coverage capacity defined by the physicochemical properties of the particles and the interface generated defined by the hydrodynamic factors of the production process. This is illustrated in Figure 5.

![Figure 5: Coverage capacity and interface generation of Pickering emulsions](image)

In a stirred tank, the dispersion of the dispersed phase droplets and the suspension of the particles in the system are important. The flow produced by the impeller affects the distribution of the particles and drops throughout the tank. Droplet breakup occurs predominantly in areas around the impeller because of the intense turbulence and high shear generated in this area (Hemrajani et al., 2004). This concept is illustrated in Figure 6. Particles are also able to adsorb onto the newly generated interfaces in these zones. Away from the impeller, coalescence occurs as a result of
the lower turbulence and shear (Wichterle, 1995). The drops are able to remain in contact long enough for them to coalesce. The baffles prevent vortex formation and provide axial motion. When the coverage potential is constant and sufficient in a Pickering emulsion system, the resulting droplet size distribution in the stirred tank is dependent on the selection, placement and operation speed of the impeller.

Figure 6: Pickering emulsion formation in stirred tank

1.4. Thesis Motivation and Structure

The focus on the studies carried out on Pickering emulsions has been on the effect of physicochemical properties on the form and stability of emulsions. There is very limited literature on the effect of hydrodynamics on emulsion properties. In several studies, Pickering emulsions are produced using crude hand-shaking methods or high energy intensive homogenizers and ultrasonicators. There are no studies on producing these emulsions in a large scale with low energy agitated systems such as
a stirred tank. It has been proposed by Tsabet and Fradette (2015) but so far, there has been no comparison of different impeller types and hydrodynamic conditions within the tank. In this study, it is aimed to investigate the effects of several hydrodynamic parameters on the final drop size distribution of a concentrated, coalescing Pickering emulsion system in a stirred tank. It also aimed to gain an insight into the processing effects on the Pickering emulsion emulsification. This is achieved by using two different impeller types, a PBT and a RT, at two sizes - T/2 and T/3. The physicochemical properties of the system were set constant to ensure that the results are only affected by the applied hydrodynamic conditions.

The next chapters in this thesis consist of the experimental method, results and summary of this study. The results of the studies are split into two chapters. Chapter 3 discusses the results of the investigation of different hydrodynamic parameters, namely tip speed, power per mass, Reynolds number and Weber number. The effects of these parameters on the resulting average droplet size and droplet size distribution are analyzed and presented. The conclusions of the findings are given in the chapter.

Chapter 4 takes a look at the processing effects on the Pickering emulsion production during emulsification. It discusses the effect the change of impeller speed on the drop size in terms of the trend of the average drop sizes at each speed and the distribution curve of the evolved drops at each speed. It investigates how the change of impeller speed over time affects the droplet size of Pickering emulsions. The speeds were increased and decreased during emulsification to check for speed hysteresis. The conclusions are also given within the chapter.

Chapter 5 summarizes the work done on the thesis and gives a general conclusion to the findings. It also suggests future works that can be done to improve and implement the results of the study.
2.1. Materials

In the emulsion formulation, hydrophilic glass beads (Sovitec Microperl) with an average diameter \((d_{50})\) of 20 μm were used as the stabilizing particles. A crude setup to determine the contact angle of the glass beads using a static test based on the Laplace equation for capillary rise in a tube was implemented to approximate the contact angle of the glass beads. This method was detailed by Galet et al. (2010). The physical properties of the particles are given in Table 3. The particles are spherical as confirmed by the microscopic image given in Figure 7.

Table 3: *Physical properties of the glass beads*

<table>
<thead>
<tr>
<th>Product name</th>
<th>Sovitec Microperl hydrophilic glass beads</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter ((d_{50}))</td>
<td>20 μm</td>
</tr>
<tr>
<td>Density</td>
<td>2.52 g/cm³</td>
</tr>
<tr>
<td>Chemical Composition</td>
<td>Soda lime glass</td>
</tr>
<tr>
<td>Contact Angle</td>
<td>62° ± 4</td>
</tr>
</tbody>
</table>
Distilled water was used as the continuous phase and 100 cSt silicon oil (XIAMETER® PMX-200, Dow Corning) was used as the dispersed phase. The physical properties of the oil are given in Table 4. This oil was chosen because silicon oil has been widely used in emulsion studies. The one study available in the literature that investigates the production of Pickering emulsions in a stirred tank by Tsabet and Fradette (2015) also utilized silicon oil and showed the effect of viscosity on the droplet size and recommended that lower viscosity oils should be preferred. They found that the smaller droplets were produced with lower viscosities and that the droplet sizes were similar with silicon oils having viscosities below 500 cSt. An oil to water ratio of 30% (v/v) was used in the experiments with a 48% (w/w) particle-to-oil ratio. The oil-in-water interfacial tension was measured with a pendant drop technique as 59.748 mN/m. For the mixing time experiments, Bromocresol Purple (Sigma Aldrich) was used as the indicator, 10 M hydrochloric acid (Isolab) as the acid and 10 M sodium hydroxide (Isolab) as the base.
2.2. Tank Set-up

The experiments were carried out in a 1L glass beaker of 9.9 cm diameter (T). The dimensions of the tank configuration are given in Figure 8. Full baffles were used to prevent vortex formation and to ensure maximum mixing. The liquid height (H) was set to be equal to the tank diameter (T). Two impellers were used to generate different flow patterns: a Rushton Turbine for radial flow pattern and a down-pumping 45° Pitched Blade Turbine (PBT) for mixed flow pattern. Two sizes of each impeller were used: T/2 and T/3. The impellers were 3D printed with polyamide material. The impeller dimensions are given in Table 5. The printed impellers of the two different sizes and types are shown in Figure 9. The off-bottom clearance of the impeller (C) was selected as T/3. The agitation was provided by an overhead stirrer motor (IKA Microstar 7.5 control).

### Table 4: Physical properties of the dispersed phase

<table>
<thead>
<tr>
<th>Product name</th>
<th>XIAMETER® PMX-200 Silicone Fluid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>100 cSt</td>
</tr>
<tr>
<td>Density (25°C)</td>
<td>0.964 g/cm³</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.4030</td>
</tr>
<tr>
<td>Surface tension (25°C)</td>
<td>20.9 mN/m</td>
</tr>
</tbody>
</table>
Figure 8: Stirred tank configuration

Table 5: Impeller specifications

<table>
<thead>
<tr>
<th></th>
<th>Rushton turbine</th>
<th>Pitched blade turbine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impeller diameter (D)</td>
<td>T/3, T/2</td>
<td>T/3, T/2</td>
</tr>
<tr>
<td>Disc diameter</td>
<td>0.66D</td>
<td>-</td>
</tr>
<tr>
<td>Disc thickness</td>
<td>0.011D</td>
<td>-</td>
</tr>
<tr>
<td>Blade thickness</td>
<td>0.011D</td>
<td>0.011D</td>
</tr>
<tr>
<td>Blade length</td>
<td>0.25D</td>
<td>0.4D</td>
</tr>
<tr>
<td>Blade width</td>
<td>0.2D</td>
<td>0.2D</td>
</tr>
<tr>
<td>Hub outer diameter</td>
<td>0.16D</td>
<td>0.25D</td>
</tr>
<tr>
<td>Hub inner diameter</td>
<td>0.08D</td>
<td>0.12D</td>
</tr>
</tbody>
</table>
2.3. Emulsification Procedure

In producing the emulsions, 100 g of solid glass beads (48% (w/w) particle-to-oil ratio) was added into the tank. This amount of particles was chosen so that there would be excess particles in the system and the final drop sizes would be controlled by the interface generated rather than the coverage potential. Then, the impeller position was set and water was added. The particle/water mixture was stirred for 10 minutes. This was done to wet the particles and break up aggregates. For the two impeller sizes, fixed speeds lower than the emulsification speeds were chosen to pre-disperse the particle/water mixture: 550 rpm for T/2 impellers and 1100 rpm for T/3 impellers. These speeds were selected to ensure the suspension of all particles with minimum air entrainment for both impeller types. Silicon oil was then added in a single batch and the speed was increased to the desired emulsification speed.

Samples were taken from the tank at a position halfway between the impeller and the liquid surface in the axial direction and shaft and tank wall in the radial at desired time intervals while the impeller is rotating. Figure 10 shows the microscopic image
of the Pickering emulsion droplet produced. All experiments were performed at least twice to ensure reproducibility of the results. The average of the data points was reported in the figures and the reproducibility is reported with error bars. The error bars are given as difference from the mean. This means that the largest data point obtained is at the top point of the error bar and the smallest data point is at the bottom of the error bar.

**Figure 10:** Pickering emulsion droplet

### 2.4. Speed Selection

In determining the viscosity of the emulsion system, Einstein’s viscosity equation was considered to connect the relative viscosity with the volume fraction of the dispersed phase.

\[
\mu = \mu_c(1 + 2.5V)
\]

Where \(\mu\) is the emulsion viscosity and \(\mu_c\) is the continuous phase viscosity. \(V\) is the volume fraction of the dispersed phase. This equation is valid for emulsions with small concentration of dispersed spherical drops. However, it is inadequate for higher volume fraction and significant deviations occur. For the volume fraction of
0.3 used in the experiments in this study, a modified viscosity model was used. It was adapted from a study by Roscoe et al. (1952) for high concentration dispersions of spheres of equal size.

\[ \mu = \mu_c(1 - 1.35V)^{-2.5} \]  \hspace{1cm} (9)

This equation was sufficient to model the viscosity of the particle-oil-water emulsion system, with the assumption that the excess particles constituted the continuous phase and that the emulsion droplets were spherical and of equal size.

Emulsification is most effective in the turbulent regime for the oil and aqueous phases used in this study. For stirred tanks, this occurs at Reynolds numbers (Re=ND^2/\nu) greater than 2x10^4. Speeds were selected to correspond with the turbulent regime. In addition to that, the just drawn down speed (NJD) of the system was considered. NJD is the speed at which the dispersed phase is completely drawn into the continuous phase. Skelland et al. (1978). After visual observation of these speeds for different impeller configurations, speeds were selected above the NJD to ensure that all the oil is used for emulsion production.

Another limiting speed that was considered was the air entrainment speed (NE). NE is the speed at which a significant amount of air bubbles enter and remain in the tank volume. The method implemented to determine these speeds was detailed by Bhattacharya et al. (2007). In this method the air bubbles entering the tank volume are visually observed. Air entrainment cannot be completely eliminated during emulsification, but it was observed that at impeller speeds slightly above NE the drops were not affected by the small presence of the air bubbles. The presence of air during pre-mixing was more problematic; therefore, the pre-dispersion speeds were selected below NE for all cases.

2.5. Droplet Size Measurement
Particle and droplet size analysis was done using Malvern Mastersizer 3000. The equipment is based on the principles of static light scattering. The small particles scatter light at large angles and large particles scatter light at small angles. The Mastersizer records the light scattered by the droplets or particles in the samples and returns its corresponding size distribution according to light-scattering theories. The Mastersizer used the Fraunhofer theory to present the droplet size distribution in terms of volume distribution. The Fraunhofer theory works well for particles larger than 10 µm (Xu, 2000).

In measuring the drop size obtained in a particular experiment, a sample was taken from the tank and stored in a vial for at least 2 hours. This was done to allow the excess particles to settle at the bottom of the vial so the measured sample contains a minimal amount of particles. The drops were then analyzed in the Mastersizer. Each sample was analyzed at least twice. For each analysis, the Mastersizer was set to perform 5 measurements. The averages of all measurements were calculated and the volume averaged diameter (d_{43}) was reported. The d_{43} is the most representative diameter obtained by light scattering techniques (Rawle, 1993). Also, the d_{43} is not as influenced by the excess particles in the system as the d_{32}. The size distribution of the glass beads particles obtained from the Mastersizer is given in Figure 11 and a sample distribution of the emulsion droplet sizes is given in Figure 12. The emulsion droplet size distributions are generally unimodal. A slight peak may be observed in the particle size range and this is as a result of the presence of some excess particles in the sample. The d_{43} diameter cancels out the effect of the excess particles and gives a more accurate droplet size representation.
2.6. Mixing Time Analysis

Mixing time is the time taken for a stirred tank to achieve a certain degree of homogeneity. A novel procedure detailed by Cabaret et al. (2007) was implemented to determine the macromixing time of the configurations tested. This procedure consists of two parts. The first part is video recording a decolorization process in the tank using a fast acid-base indicator reaction. An acid-base ratio greater than 2 was
used to obtain macromixing, as recommended by Cabaret et al. (2007). Then, an image analysis technique was implemented on the recorded videos to obtain a mixing curve. The details of each part are given below.

The color change in the tank was recorded with a Canon EOS 100d (25 fps) camera. A solution of bromocresol purple (0.08% w/w in water) was used as the indicator. An injection sample was prepared by mixing a sample of the tank mixture with 2ml of 10M HCl. The injection sample volume was set to be 0.5% of the total tank volume. This is for the injection sample to have a density close to density of the emulsion in the tank so that a reproducible mixing curve can be obtained. At the beginning of the experiment, 1 ml aqueous 10 M NaOH was added to the tank mixture. 20 ml of the bromocresol purple solution was added to color the mixture purple. When a steady hydrodynamic state was reached in the tank, the camera was turned on. The acidic injection sample was added and the color change was recorded. For reproducibility purposes, the acid was always added rapidly at the same location on the tank surface. Since it is easier to follow the change of darker colors to lighter colors, the change of the tank volume from purple (basic) to yellow (acidic) was followed.

The video was split into frames using VLC software. The frames and colour change of a sample experiment are shown in Figure 13.

![Figure 13: Frames of color change in mixing time experiment](image)

Each frame was converted to a portable pixel map (ppm) format and was represented by a matrix of pixels which can be separated into the red, green and blue (RGB)
components. For each pixel, an individual threshold on an RGB component is defined in order to separate an ‘unmixed’ pixel from a ‘mixed’ one. For bromocresol purple, it was reported by Cabaret et al. (2007) that the green component should be followed and a threshold value ratio of 50% should be used. Since the green component is followed, a pixel will be considered mixed as soon as its green component is greater than the threshold value. For each image sampled from the video, the number of mixed pixels ($N_{\text{mixed}}$) was counted and then the ratio of $N_{\text{mixed}}/N_{\text{total}}$ over time was plotted to obtain a mixing curve, where $N_{\text{total}}$ is the total number of pixels. This ratio represents the ‘mixedness’ of the system. 95% was chosen as sufficient homogeneity for the system. For each experiment, a mixing curve such as the one shown in figure was obtained and the time it took to obtain 95% ‘mixedness’ was observed.

![Mixedness vs Time](image)

*Figure 14: Mixing time curve*
CHAPTER 3

THE EFFECT OF HYDRODYNAMIC PARAMETERS ON THE DROPLET SIZE OF PICKERING EMULSIONS IN BAFFLED STIRRED TANKS

3.1. Results and Discussions

Pickering emulsions were produced with the emulsification procedure described earlier and results are presented comparing the performance of two impeller types at two different sizes: pitched blade turbine (PBT) and the Rushton turbine (RT) at T/2 and T/3 diameter. The physicochemical properties of the system were set constant to ensure that the results are only affected by the applied hydrodynamic conditions.

This chapter focuses on investigating the effects of hydrodynamic parameters namely the tip speed, power per mass, Reynolds number and Weber number on the resulting emulsion droplet size. The effects of these parameters on the final droplet size distribution of a concentrated, coalescing Pickering emulsion system are analyzed and presented. The presence of particles in the system are expected to affect the flow in the tank and the particle adsorption capacity should affect the resulting droplet sizes.

3.1.1. Selection of Emulsification Time

Preliminary experiments were carried out using one of the working speeds for the emulsification process to determine the time it would take for the droplets to stabilize and reach an equilibrium size. The T/3 impellers were tested at 1625 rpm and the T/2 impellers were tested at 954 rpm. Samples were taken every hour for 6 hours for each experiment. Figure 15 shows the droplet size evolution with time for the T/3 impellers. There is a 17% range of change of droplet size with time and the droplets seem to be stabilized after the 3rd hour. Figure 16 shows the change in droplet size with time for the T/2 impellers. There is a 13% and 9% range of change
in droplet size with time for the PBT T/2 impeller and the RT T/2 impeller respectively. The droplets also seem to be stabilized after the 3rd hour. It is worth noting that the RT T/2 impellers is least affected by time and it reaches equilibrium size faster than the other impellers.

*Figure 15: Change in droplet size with time for the T/3 impellers*

*Figure 16: Change in droplet size with time for the T/2 impellers*
As a result of these preliminary tests, it was decided that the experiments to determine the effect of the hydrodynamic parameters would be run for 3 hours for every impeller. This serves to standardize the results of the emulsification experiments and give adequate time for the droplets to reach an equilibrium average size.

### 3.1.2. The Effect of Tip Speed on Droplet Size

Droplet sizes evolved at three working tip speeds ($\pi ND$) for each impeller were plotted on Figure 17. As the tip speed increases, a slight decrease is observed in the droplet size for all impellers. Comparison of the two types of impellers can be done best at the same tip speed. Two tip speeds are common for both sizes of the RT and the PBT impellers: 155 and 165 m/min. As given in Figure 18, both sizes of the RT impellers produce smaller droplet sizes than the PBT impellers at the same tip speed. These differences could be a result of the higher power number of the RT impeller. The power number of the RT impeller (5.5) is about four times that of the PBT impeller (1.3) in the fully turbulent regime, which is the case under consideration (Chapple et al., 2002). Therefore, the RT impeller has more energy dissipated around the impeller zone. This enhances droplet breakup and allows for the formation of smaller and more numerous droplets.
Figure 17: The effect of tip speed on droplet size with different impellers

Figure 18: Comparison of droplet sizes obtained with four impellers at the same tip speeds

This point can be further illustrated using the equation for energy dissipation:
\[ \varepsilon = \frac{P}{\rho V_{\text{swept}}} = \frac{N_p \rho N^3 D^5}{\rho \pi D^2/4 \cdot D/5} \]

\[ \varepsilon \propto N_p N^3 D^2 \]

For the same size of the two types of impellers at the same tip speed, the only difference in energy dissipation is the power number. This once again indicates that the power number is a controlling factor: the higher the power number, the smaller the droplet sizes. The size of the impeller can be considered as the next controlling factor: the larger the impeller diameter, the smaller the droplet sizes. This is why amongst the same type impellers, at the same tip speed, the T/2 impeller produced smaller droplets than the T/3 impeller.

The data in Figure 17 shows that PBT T/3 impeller produces the largest droplet sizes. The error bars on each data point in Figure 17 are also large. Flow in the tank with a PBT T/3 impeller was observed to have several dead zones and poor circulation. The fluid mass tends to spend more time in the zones around the baffles, liquid surface and vessel wall where shearing is non-existent. This was observed at all speeds used for the other experiments in this paper. This could be the reason of the large droplet sizes. Based on this data PBT T/3 impeller proves to be an unfavorable impeller for producing Pickering emulsions.

In comparing the performance of different impellers, droplet size distribution or the span of distribution should also be considered. Figure 19 and Figure 20 present this information. Figure 19, at \( V_{\text{tip}} = 155 \) m/min, shows that the span of distribution is the largest for the PBT T/3 impeller. RT T/3 impeller gives the smallest span; therefore, the narrowest droplet size distribution. A similar trend is seen in Figure 20, for \( V_{\text{tip}} = 165 \) m/min. PBT T/3 impeller gives the largest span, but this time the spans of the RT T/2 and PBT T/2 impellers are closer to that of the PBT T/3 impeller and the span of RT T/3 impeller is even smaller. This shows that increasing the tip speed may result in a decrease in the average droplet size, but for the large impellers the polydispersity of the emulsion increases. The PBT T/3 impeller proves to be an
outlier indicated by the large span of distribution for all cases. This shows once again that the flow field produced by a PBT T/3 impeller is not adequate for production of Pickering emulsions.

Figure 19: Droplet size distributions at tip speed 155 m/min

Figure 20: Droplet size distribution at tip speed 165 m/min

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The differences in the break-up of droplets by the RT impeller and PBT impeller can be better understood based on an analogous study done by Martin et al. (2008) comparing the bubble breakup mechanisms of the two impellers. For a PBT impeller, they observed that the geometry of the impeller does not allow for the bubbles to gather around the blades and that the main breakup mechanism consists of leading the bubbles to the edge of the blades where they are cut. The bubbles can also sometimes avoid the blades. When applied to a Pickering emulsion system in which the dispersed phase droplets need to be broken and solid particles need to adsorb onto the interface, the breakup mechanism of the PBT impeller is not efficient. Since the droplets do not gather around the impeller, the adsorption efficiency with this impeller will be low because the particles and the droplets are not able to spend sufficient time together. The breakup efficiency of the impeller is low as well because droplets might avoid the impeller and not breakup. For the RT impeller, Martin et al. (2008) observed that the impeller disc has a significant effect on the bubble breakup mechanism. The bubbles are retained below the disc before the impeller rotation moves them to the blades where they are broken. As a result, the particles in a Pickering emulsion system are able to spend more time to adsorb onto the droplet interface before the droplet breaks. Therefore, adsorption efficiency and breakup efficiency of the RT impeller is higher than that of the PBT impeller. This leads to the RT impeller producing smaller droplets than the PBT impeller.

Additionally, radial flow impellers such as the RT impeller tend to generate higher shear than axial and mixed flow impellers such as the PBT impeller. They generate higher shear in terms of higher level of turbulence around the impeller and the formation of trailing vortices. Trailing vortices are a pair of counter-rotating vortices generated behind the lower and upper parts of the impeller blade (Escudie et al., 2004). They provide additional turbulence to the flow of a RT impeller and the high level of turbulence around the impeller allows for more effective droplet breakup. On the other hand, PBT impellers have higher pumping capacity than the RT impeller. The pumping capacity is a measure of the amount of liquid leaving the
impeller region per unit time. The ratio of the power number to the flow number of an impeller ($N_P/N_Q$) is an indicator of its pumping capacity. The lower the ratio, the higher the pumping capacity (Chudacek, 1985). A high pumping capacity indicates the frequency at which the liquid volume can move around the tank. Despite the PBT impeller having a higher pumping capacity than the RT impeller, the RT impeller produces smaller droplets. It can be said then that in producing smaller droplets, high shear generation is more critical than high pumping capacity.

3.1.3. The Effect of Power/Mass on Droplet Size

The power per mass based on the impeller swept volume approximates the energy dissipated at the impeller zone. The impeller zone is where the oil is broken into droplets and uncovered or partially covered droplets are broken into smaller droplets; therefore, the energy dissipation around the impeller can be a good indicator of the minimum droplet size that can be achieved in the tank.

Figure 21 illustrates the effect of power per mass on the droplet sizes produced by different impellers. As the power per mass increases, in general there is a decrease in the droplet sizes. This is expected because increasing the amount of energy dissipated should increase the droplet breakup rate and produce smaller droplets if particle adsorption can be achieved.
In Figure 22, the droplet sizes produced by the four impellers are compared at the same average energy dissipation rate. It is clear that the impellers are grouped based on their sizes: the T/2 impellers produce smaller droplets than the T/3 impellers. PBT T/3 impeller again produces the largest droplets, but this time RT T/3 impeller data approaches the PBT T/3 data. The difference between the larger impellers is quite small, indicating that at the same power per mass the droplet sizes obtained by the T/2 impellers are not affected by the type of the impeller. This also means that the power per mass can be the main parameter that determines the droplet size for the larger impellers.

Figure 21: The effect of power/mass on droplet size with different impellers
The T/2 impellers perform better because, as shown in Figure 23, the T/2 impellers have a larger breakup zone. Therefore, there is more space within the tank for droplet breakup and particle adsorption. The size of the coalescence zones which are away from the impeller zone is also decreased; therefore, the droplets also have less chance of coalescence. For the T/3 impellers, there is a smaller shear zone and larger coalescence zone; therefore, they produce larger droplets than the T/2 impellers.

It is also observed that at the same impeller size and power per mass, the RT impeller produces smaller droplets than the PBT impeller. For T/3 impellers, the difference is significantly large. This is due to the greater shear generation capacity of the RT impeller in terms of higher turbulence generated in the impeller zone and the more effective droplet breakup and particle adsorption mechanism. For T/2 impellers, the difference is not significant. The RT impeller still has higher shear generation capacity. It has been reported that as the impeller size increases for PBT impellers, the radial component of their flows becomes more significant and they behave like radial flow impellers (Hemrajani and Tatterson, 2004). Therefore, the
PBT T/2 impeller has closer shear generation capacity to the RT T/2 impeller than their T/3 counterparts.

In previous studies on conventional liquid-liquid dispersions, Pacek et al. (1999), Musgrove and Ruzkowski (2000) and El-Hamouz et al. (2009) observed that at the same energy dissipation rate, low shear impellers (with lower power numbers) tend to produce smaller droplets than high shear impellers (with higher power numbers). This is contrary to observations of these experiments. The high shear impeller; RT, produced smaller droplet sizes than the low shear impeller; PBT. This is because the droplet breakup mechanism of the RT impeller allows for a higher adsorption efficiency of the particles as described earlier.

Figure 24 and Figure 25 show the span of distribution of all the impellers at the same power/mass. The two figures show the same trend. The PBT T/3 impeller has the highest span, therefore, it has the widest distribution. This is a result of the poor circulation mentioned earlier. The RT T/3 impeller once again gives the smallest span; therefore, the narrowest droplet size distribution. The spans of distribution obtained with the large RT and PBT impeller are between the small PBT and RT impeller, and they are close to each other.
Figure 24: Droplet size distribution at power/mass 250 W/kg

Figure 25: Droplet size distribution at power/mass 305 W/kg
3.1.4. The Effect of Reynolds Number on Droplet Size

Figure 26 shows the droplet sizes obtained with the four impellers tested at varying Reynolds numbers. The RT impellers produce smaller droplets than the PBT impellers. This is expected because it was noted earlier that the Rushton turbines dissipate more energy at the impeller region than the PBT impellers. They also generate more shear for the breakup of droplets and formation of smaller droplets. A similar observation was made for the tip speed results. It is observed in Figure 26 and Figure 27 that at the same Reynolds number, the T/3 RT impeller produced smaller droplets than the T/2 RT impeller. The T/3 PBT impeller also produced relatively close droplet sizes to the T/2 PBT impeller: within 12% difference at the lower Reynolds numbers. At increased Reynolds numbers, the difference may increase up to 20% as the T/3 PBT behaves unexpectedly. Note that, for the same impeller type, the T/3 impeller required much higher rotational speeds to have the same Reynolds number with the T/2 impeller. This means much higher energy dissipation around the impeller zone. This explains how the T/3 RT impeller produces smaller droplets than the T/2 RT impeller.

The droplet size is also observed to decrease as the Reynolds number increased. This is expected because increasing the Reynolds number leads to increased turbulent fluctuations and energy dissipation. This in turn, decreases the droplet size.
Figure 26: The effect of Reynolds number on droplet size

Figure 27: Comparison of droplet sizes obtained with four impellers at the same Reynolds number
In terms of energy dissipated, since

$$\text{Re} = \frac{ND^2}{u}$$

$$\epsilon \propto N_p N^2 \text{Re}$$

At the same Reynolds number, the energy dissipated has a high dependency on the impeller speed. The energy dissipated by the T/3 impeller (2.5 times the speed of the T/2 impeller) is evidently much higher than that of the T/2 impeller. This is the reason the T/3 impeller produced smaller droplets. What about the effect of the breakup zone size? It was observed earlier that at the same energy dissipated, the breakup zone size is a controlling factor in the droplet size evolution. The bigger the breakup zone, the smaller the droplet sizes. The results from these experiments show, however, that the energy dissipated and shear generated is more critical to droplet size evolution than the breakup zone size. This is evident in the fact that the T/3 RT impeller has a smaller breakup zone but still produces smaller droplets with its higher energy dissipation at the impeller zone.

The T/3 PBT impeller flow still has dead zones and poor circulation. For this reason, it is still expected to produce the largest droplet sizes. It is observed that the T/2 and T/3 PBT impellers produce droplet sizes close to each other. This is because the PBT T/2 impeller ultimately dissipated low energies as a result of the relatively lower speeds.

Figure 28, Figure 29 and Figure 30 show the span of the droplet size distributions of the impellers at the same Reynolds number. At the low Reynolds number, the PBT T/3 impeller is seen to have the widest distribution as expected. As the Reynolds number increased, however, the polydispersity with the other impellers increases and unexpectedly, the PBT T/3 impeller has the lowest span.
Figure 28: Droplet size distribution at Reynolds number 24000

Figure 29: Droplet size distribution at Reynolds number 28000
3.1.5. The Effect of Weber Number on Droplet Size

While the parameters considered until now are general parameters for mixing applications, the Weber number is specific to immiscible liquid-liquid systems. Figure 31 and Figure 32 show that at the same Weber number, the RT T/2 impeller produced by far the smallest droplets and the droplet size is not affected by the increasing Weber number. It is followed by the RT T/3 and PBT T/2 impeller as these two impellers produce almost the same size droplets. At the last two highest Weber numbers, the size of the droplets obtained by the RT T/2 impeller are not affected by the Weber number. With PBT T/2 impeller however, the droplet sizes continue to decrease with increasing Weber number. At the highest Weber number of 695 the PBT T/2 impeller produces smaller drops than the RT T/3. The PBT T/3 impeller still produces the largest droplet sizes as a result of poor circulation reasons mentioned earlier.
Figure 31: The effect of Weber number on droplet size

Figure 32: Comparison of droplet sizes obtained with four impellers at the same Weber number
The trend observed in these experiments indicates a point where the breakup zone becomes more controlling than the generated shear and dissipated energy. This can be said because as the Weber number increased, the PBT T/2 impeller gradually produced smaller droplets than the RT T/3 impeller. This point is further illustrated in Figure 33, Figure 34 and Figure 35. In Figure 33, at the Weber number 445, the curves of the PBT T/2 impeller and RT T/3 impeller are close to each other with the RT T/3 curve indicating a slightly smaller and narrower droplet size distribution. The PBT T/2 impeller has a wider distribution because of its relatively lower speed. In Figure 34, We=575, the curves of the PBT T/2 and RT T/3 impellers are even closer to each other. This time, the PBT T/2 curve indicates a slightly smaller and narrower droplet size distribution than the RT T/3 curve. Finally, Figure 35, We=695, shows the curves of the PBT T/2 and RT T/3 impellers move away from each other. The PBT T/2 curve indicates an even smaller and narrower droplet size distribution than the RT T/3 curve. At this point, the effect of the breakup zone can be said to have taken more importance than the effect of the power dissipated in producing smaller droplet sizes.

Figure 33: Droplet size distribution at Weber number 445
Figure 34: Droplet size distribution at Weber number 575

Figure 35: Droplet size distribution at Weber number 695
3.1.6. Comparison of the Effects of the Hydrodynamic Parameters

Four common hydrodynamic design parameters for stirred tanks were selected to investigate their effect on the droplet size of Pickering emulsions. Four impellers were used: RT T/2, RT T/3, PBT T/2, PBT T/3. The effects of these parameters are compared in this section.

The results revealed some important considerations: the power number, energy dissipation around the impeller, shear generation capacity, droplet breakup and particle adsorption efficiency, breakup and coalescence zone sizes, impeller speed and pumping capacity. The RT impeller was characterized with a better droplet breakup and particle adsorption mechanism, higher shear generation capacity and a higher power number than the PBT impeller. The PBT impeller was characterized with a higher pumping capacity than the RT impeller. The T/2 impellers had a larger shear zone and smaller coalescence zone than the T/3 impellers. The T/3 impellers required higher impeller speeds than the T/2 impellers.

Table 6 gives an overview of the comparison of the values of the energy dissipated and impeller speeds at the same hydrodynamic parameters.

Table 6: Comparison of energy dissipated and impeller speeds at the same hydrodynamic parameter

<table>
<thead>
<tr>
<th>Hydrodynamic parameter</th>
<th>Energy dissipated (ε) RT vs PBT</th>
<th>Energy dissipated (ε) T/2 vs T/3</th>
<th>Impeller speed (N) T/2 vs T/3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Same Tip speed</td>
<td>$\varepsilon_{RT} = 4.23\varepsilon_{PBT}$</td>
<td>$\varepsilon_{T/2} = 0.66\varepsilon_{T/3}$</td>
<td>$N_{T/2} = 0.67N_{T/3}$</td>
</tr>
<tr>
<td>Same Power per mass</td>
<td>$\varepsilon_{RT} = \varepsilon_{PBT}$</td>
<td>$\varepsilon_{T/2} = \varepsilon_{T/3}$</td>
<td>$N_{T/2} = 0.76N_{T/3}$</td>
</tr>
<tr>
<td>Same Reynolds</td>
<td>$\varepsilon_{RT} = 4.23\varepsilon_{PBT}$</td>
<td>$\varepsilon_{T/2} = 0.2\varepsilon_{T/3}$</td>
<td>$N_{T/2} = 0.44N_{T/3}$</td>
</tr>
<tr>
<td>Same Weber</td>
<td>$\varepsilon_{RT} = 4.23\varepsilon_{PBT}$</td>
<td>$\varepsilon_{T/2} = 0.36\varepsilon_{T/3}$</td>
<td>$N_{T/2} = 0.54N_{T/3}$</td>
</tr>
</tbody>
</table>
The experiments at the same tip speed showed the effect of the difference in the power number of the impellers. The impeller with higher power number and shear generation capacity: the RT impeller, produced smaller droplets. This is because the RT impeller has more energy dissipated at the impeller region as shown in Table 6. The size of the coalescence zone also played a critical role in the resulting droplet size. Amongst the same type impellers, the T/2 impeller produced the smaller droplets. They dissipated more energy in the impeller zone and required lower speeds to do so. The T/2 impellers also have a larger shear zone and a smaller coalescence zone. Therefore, there is more space within the tank for droplet breakup and particle adsorption. As a result, the droplets have less chance of coalescence. This effect was confirmed in the power per mass experiments. At the same power per mass (energy dissipated), the T/2 impellers produced smaller droplets than the T/3 impellers regardless of the impeller type. The more effective droplet breakup and particle adsorption mechanism of the RT impeller allowed for it to produce smaller droplets than the PBT impeller at the same size. It was observed that a higher energy dissipation rate, effective breakup mechanism and a small coalescence zone size yields the smallest, most stable droplets.

The experiments at the same Reynolds number showed the dependency of the resulting drop sizes on the impeller speed. The RT T/3 impeller produced the smallest droplets in this set of experiments. A much higher speed was required by the RT T/3 impeller to achieve the same Reynolds number with the RT T/2 impeller. As a result, the energy dissipated by the T/3 impeller is much higher than that of the T/2 impeller. The results show that the energy dissipated is more critical to the resulting droplet size than the coalescence zone size. The Weber number experiment results then indicated that there could be a point where the effect of the coalescence zone becomes more important than the effect of the power dissipated in producing smaller droplets.
The PBT T/3 impeller flow was characterized by dead zones and poor circulation. The tank volume was not fully mixed and area around the liquid surface, tank wall and behind the baffles could be observed to stagnant with minimal movement. This was observed even at the highest possible speed of the motor. For this reason, the PBT T/3 impeller produced large droplets with large and irregular distributions.

The high pumping capacity of the PBT impeller was not sufficient to give it an advantage over the RT impeller. It performed best when it was compared at the same power per mass because of the same energy dissipation around the impeller. Therefore, pumping capacity is not as critical as high shear generation in the formation of smaller droplets.

3.2. Conclusions

In most studies, dilute emulsions with low dispersed phase fractions were investigated. These emulsions are either stabilized by surfactants or not stabilized at all. The objective of this study was to develop an understanding of the effect of certain hydrodynamic parameters on the production of concentrated Pickering emulsions with a high dispersed phase fraction. In producing Pickering emulsions, the success of the droplet formation and stabilization depends on the particle coverage potential and the interface generated by the hydrodynamic conditions. The hydrodynamic conditions affect both the liquid-liquid dispersion and the particle suspension. The droplet break-up mechanism and droplet retention ability of the impeller is key to the performance of the impeller in producing smaller drop sizes. It was noted that the smaller and narrower the droplet size distribution, the more stable the formed emulsion would be. The effect of the flow behavior and size of the RT impeller and PBT impeller on the resulting droplet size distribution was observed and the following conclusions were reached:

- The controlling factors of the evolved droplet size distribution are the energy dissipated at the impeller zone and the size of the breakup zone. Higher energy dissipated leads to smaller droplets. Larger breakup zones
also lead to smaller droplets. Zhou and Kresta (1998) and Musgrove and Ruszkowski (2000) stressed that the final drop sizes of liquid-liquid dispersions must be related to the hydrodynamics of the droplet breakup zone. This also applies to the coalescing system with the presence of particles studied in this paper.

- At the same tip speeds, the RT impellers produced smaller droplets than the PBT impellers. This is because the RT impeller has a higher power number and better dispersion geometry than the PBT impeller. Therefore, if tip speed is used as a scaling factor, the impeller with the higher energy dissipation (power number) and better dispersion geometry should be used.

- At the same power per mass (energy dissipated), the breakup zone is critical and the impellers with larger diameters (T/2) regardless of the impeller type should be preferred. The RT impeller should be preferred because of its better dispersion geometry and lower speed requirement to reach the same power per mass as the PBT impeller.

- At the same Reynolds number; due to the high dependency of the energy dissipated on the impeller speed, the T/3 RT impeller produced the smallest droplets due to its relatively higher speed than the T/2 RT impeller.

- At the same Weber number, the T/3 RT and the T/2 PBT impellers showed that after a point, the coalescence zone can be more controlling than the energy dissipated in terms of producing smaller drop sizes.

- The T/2 RT impeller was found to be the most effective impeller; having both high energy dissipation and smaller coalescence zone. Its effective dispersion geometry also allowed for it to produce the smallest droplets.
• The T/3 PBT impeller was found to be the least effective impeller as a result of its poor circulation. It also had low energy dissipation and larger coalescence zone compared to the other impellers.
CHAPTER 4

THE EFFECT OF THE CHANGE OF IMPELLER SPEED ON THE DROPLET SIZE DISTRIBUTION OF PICKERING EMULSIONS IN A BAFFLED STIRRED TANK

4.1. Results and Discussions

In this chapter, the effect of the change of impeller speed on the drop size is discussed in terms of the trend of the average drop sizes at each speed and the distribution curve of the evolved drops at each speed. It is aimed to investigate how the change of impeller speed over time affects the droplet size of Pickering emulsions. The speeds were increased and decreased during emulsification to check for speed hysteresis.

The emulsion system is concentrated with a high dispersed phase concentration and the particle coverage is set constant. Two different impeller types, a pitched blade turbine (PBT) and a Rushton turbine (RT), at two sizes - T/2 and T/3 were used for this investigation. A mixing time analysis was then used to corroborate the results.

4.1.1. Emulsification Speed Selection and Procedure

The experiments in this part were carried out in the same manner described in the experimental procedure part. During emulsification, for every impeller, three different impeller speeds were used. They are given in Table 7. The speeds were applied for one hour each starting from the lowest speed to the highest speed. Once the highest speed was applied, the speed was decreased hourly until the lowest speed in order to study the coalescence behavior. Each experiment lasted a total of 5 hours. Samples were taken every hour while the impeller is rotating.
The lowest speeds were selected such that they were above the just drawn down speed (N\textsubscript{JD}) of the system. Therefore, the different impellers had different lowest speeds. In selecting the highest speeds, the air entrainment speed (N\textsubscript{E}) was considered. Air entrainment cannot be completely eliminated during emulsification, but it was observed that at impeller speeds slightly above N\textsubscript{E} the drops were not affected by the small presence of the air bubbles. The presence of air during pre-mixing was more problematic; therefore, the pre-dispersion speeds were selected below N\textsubscript{E} for all cases.

Table 7: Speeds selected for the experiments

<table>
<thead>
<tr>
<th>Impeller</th>
<th>Pre-dispersed speed (rpm)</th>
<th>1\textsuperscript{st} hour speed (rpm)</th>
<th>2\textsuperscript{nd} hour speed (rpm)</th>
<th>3\textsuperscript{rd} hour speed (rpm)</th>
<th>4\textsuperscript{th} hour speed (rpm)</th>
<th>5\textsuperscript{th} hour speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT T/2</td>
<td>600</td>
<td>658</td>
<td>878</td>
<td>1082</td>
<td>878</td>
<td>658</td>
</tr>
<tr>
<td>RT T/3</td>
<td>1100</td>
<td>1146</td>
<td>1528</td>
<td>1980</td>
<td>1528</td>
<td>1146</td>
</tr>
<tr>
<td>PBT T/2</td>
<td>600</td>
<td>658</td>
<td>1082</td>
<td>1500</td>
<td>1082</td>
<td>658</td>
</tr>
<tr>
<td>PBT T/3</td>
<td>1200</td>
<td>1485</td>
<td>1721</td>
<td>1980</td>
<td>1721</td>
<td>1485</td>
</tr>
</tbody>
</table>

4.1.2. Effect of the Change of Impeller Speed on Drop Size and Drop Size Distribution

Experiments were carried out to determine the effect of increasing the impeller speed over time on the drop size and drop size distribution of Pickering emulsions. The trends of the average drop sizes are given in the section and the results are further corroborated with the drop size distribution curves.

Figure 36, Figure 37, Figure 38 and Figure 39 show the transient trend followed by the drop sizes with the change in speed for the T/2 RT, T/3 RT, T/2 PBT and T/3 PBT, respectively. For all cases, as the speed increases every hour, the drop size decreases. Then on the decreasing speed path, after every hour, the drop size increases. This is the general trend observed by the impellers in this study except the
PBT T/3 impeller. For an impeller at a particular speed, a certain range of droplet size is observed regardless of the emulsification time and speed hysteresis is observed. The evolution of droplet size by varying the impeller speed is different on the increasing and decreasing speed path even though the general trend of decreasing and increasing droplet size is the same. This is referred to as speed hysteresis.

Stirring has two effects: providing the shear to elongate and break droplets, and providing the inertia to gather the drops and help them coalesce (Tolosa et al., 2006). Increased speed should favor droplet break-up over droplet coalescence because of the increase in shear and energy dissipated. The decrease of droplet size with increasing impeller speed and emulsification time is expected because as the speed increases, droplet break-up increases. Therefore, there is more interface generated for the particles to adsorb onto and stabilize the emulsion. As the speed decreases, the droplet coalescence increases because stirring then triggers inertial forces to gather the droplets and help coalescence. The relatively lower shear and circulation generated when the speed is decreased can also cause detachment of the particles from the interface. The particles are detached when the droplets are broken and are unable to adsorb back onto the surface at the same rate as when there was a higher shear and circulation. Since the droplets are gathered and are not fully covered by the particles, coalescence is encouraged.

For the RT T/2 impeller, in Figure 36, there is not much difference between the droplet sizes produced at the same speeds. The droplet sizes of the 1st and 5th hour samples are within 7% of each other and the droplet sizes of the 2nd and 4th hour samples are within 3% of each other. Very little hysteresis is observed with this impeller. In a smaller size RT impeller, the impeller shear zone size is decreased. A decrease in the shear zone may favor coalescence.
According to Figure 37, a wider difference in droplet size is observed at the low speeds. The droplet sizes of the 1st and 5th hour sample is within 21% of each other. The droplet size at the 5th hour is significantly smaller than at the 1st hour. The droplets could not coalesce enough to reach the droplet size of the 1st hour. This is because ultimately, the emulsification had been going on much longer at the 5th hour than at the 1st hour. This emulsification time played a more significant role in the droplet size evolution for the RT T/3 impeller than it did for the RT T/2 impeller.
Figure 37: Effect of T/3 Rushton turbine impeller speed on drop size

The PBT impeller is a low shear impeller compared to the RT impeller. The PBT T/2 impeller was used to see how the effect of the impeller speed on the droplet size would be affected by the change in shearing capacity. According to Figure 38, a similar trend is observed as with the RT impellers. As the speed increases every hour, the droplet size decreases and then after decreasing every hour, the droplet size increases. At the same speeds, the droplet sizes of the 1st and 5th hour sample is within 31% of each other and the droplet sizes of the 2nd and 4th hour sample is within 8% of each other. The drop size at the 5th hour is significantly larger than at the 1st hour. This shows the effect of the low shearing of the impeller because in this case coalescence is encouraged. As a result of the impeller geometry and low shearing capacity, the droplets experience inertia to gather them and help coalescence at low speeds. The longer emulsification time does not have an important role this time, due to the lower shear capacity of the PBT impeller throughout emulsification.
A smaller size PBT impeller was also investigated. As seen in Figure 39, the PBT T/3 impeller shows a different trend than the other impellers. A mixed increase and decrease trend on the droplet size is observed when increasing the speed. However, when decreasing the speed, a corresponding increasing and decreasing trend is still observed. At the same speeds, the droplet sizes of the 1st and 5th hour sample is within 11% of each other and the droplet sizes of the 2nd and 4th hour sample is within 4% of each other. The reason for this outlying trend is not fully understood and it could be as result of the flow generated by the impeller. The flow of the PBT T/3 is observed to have poor circulation and dead zones around the top of the liquid level and baffle areas. The dead zone are regions where there is no fluid movement and the droplets do not move around that area. However, similar to other impellers, a certain path is followed in the droplet evolution with change in speed regardless of the emulsification time. It also produces larger droplets at the lower speeds as a result of its low shearing capacity.
Figure 39: Effect of T/3 Pitched blade turbine impeller speed on drop size

Figure 40 shows the distribution curves obtained by the RT T/2 impeller at the same speed in corresponding hours. The span indicates the width of the distributions. At the lowest speed, 658 rpm, Figure 40a shows that the 5th hour curve has a wider distribution than the 1st hour curve. This shows the difference in how the droplets were evolved. At the 1st hour the droplet size was evolved predominantly through droplet break-up, therefore they have a narrower distribution. At the 5th hour the droplets were evolved predominantly via droplet coalescence since the speed was decreased from a higher speed at the 5th hour. Since shear is still applied, some droplet break-up still occurs. This mix of activities lead to the 5th hour droplets having a wider distribution even though it has a similar average size as the 1st hour droplets. Figure 40b shows curves of the intermediate speed, 878 rpm. The curves of the 2nd and 4th hour have relatively closer spans than the curves in Figure 40a. This shows that at the intermediate speeds droplet breakup and coalescence occur at
similar rates as when the speed was increased to it and when the speed was
decreased to it.

Figure 41, Figure 42 and Figure 43 show the width of distributions of the other
impellers at corresponding speeds. Similar patterns are observed as with the RT T/2
impeller. The 5th hour curves have wider distributions than the 1st hour curve and the
2nd hour and 4th hour curves are close to each other. The same mechanism described
for the RT T/2 impeller occurs in the formation of droplets when the speed is
increased and when the speed is decreased as the T/2 impeller.
Figure 40: Drop size distribution for RT T/2 impeller a. 658 rpm b. 878 rpm
Figure 41: Drop size distribution for PBT T/2 impeller a. 658 rpm b. 1082 rpm
Figure 42: Drop size distribution for RT T/3 impeller. a. 1146 rpm b. 1528 rpm
Figure 43: Drop size distribution for PBT T/3 impeller a. 1485 rpm b. 1721 rpm

4.1.3. Mixing Time Analysis
The mixing time of a stirred tank can be defined as the time taken to achieve a degree of homogeneity in tank volume. The mixing time is related to the circulation time of the tank, which is the time taken for the material to move around the tank. The stirred tank can be divided into two zones as shown in Figure 44: the breakup zone and the coalescence zone (Wichterle, 1995). The breakup zone is in regions close to the impeller blade. Shear is highest in this region, so the droplets can break here. The newly formed droplet interfaces in this region are also in contact with the particles, so the particles adsorb onto the interface in this zone. The coalescence zone are areas far from the impeller and close to the tank wall and liquid surface. The shear in this area is low and the droplets are able to maintain contact with each other and coalesce.

![Figure 44: Breakup and coalescence zone](image)

The amount of time that droplets spend in the breakup and coalescence zone can be estimated by the mixing time. The mixing time of the different impellers at the different speeds used to produce the emulsions in the previous section was measured. The mixing time results give additional insight to the decreasing trend observed with increased speed. Figure 45 shows the mixing times of the increasing impeller speeds for each impeller. It was observed that the mixing time decreases with increasing speed for all impellers. This confirms that increasing the speed would decrease the residence time of the droplets in the coalescence zone away from the impeller shear zone. Therefore, increasing the speed results in more circulations...
in the vessel and the droplets take less time to travel to the impeller shear zone. Decreasing the speed then increases the residence time of the droplets in the coalescence zone while also not providing as much shear as the previous speeds.

![Figure 45: Mixing time of impeller speeds for the four impellers](image)

### 4.2. Conclusions

In producing Pickering emulsions, the droplet breakup and coalescence must be considered. The suspension of particles and adsorption of particles onto the droplet interface must also be considered. The objective of this study was to observe the effect of the change of the impeller speed over time on the droplet size of Pickering emulsions. The effect was checked on two different impeller types: PBT impeller, RT impeller at two different sizes: T/2, T/3. The results were then corroborated with a mixing time analysis on all impeller speeds used. The following conclusions were reached:

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• For impellers with adequate flow, increased emulsification speed produced smaller droplets. Decreasing the emulsification speed produced bigger droplets.
• Speed hysteresis is observed in the formation of Pickering emulsion droplets.
• To increase the size of an emulsion droplet, it is recommended to use a speed lower than the initial emulsification speed unless there is inadequate flow in the tank as observed for the PBT T/3 impeller.
• The drop sizes at lower speeds are more affected by the change in impeller speed. There is a significant difference between the droplet sizes formed at the low speeds when the speed is decreased from a higher speed and the droplet sizes formed at the low speed when the speed is increased from a lower speed. At intermediate speeds, the drop sizes formed when the speed is decreased from a higher speed and the droplet sizes formed when the speed is increased from a lower speed are close to each other.
• The PBT is a low shear impeller and coalescence plays a prominent role when the impeller speed is decreased. As a result, bigger droplets are evolved when the impeller speed is decreased than its initial size at the same low speed.
• Increasing the impeller speed decreasing the mixing time of the tank. Therefore, the droplets are able to circulate back to the breakup zone more often and spend less time in the coalescence zone. The drops spend more time in the breakup zone where droplet breakup and particle adsorption can occur. As a result, increasing the impellers speed leads to smaller droplets.
CHAPTER 5

SUMMARY, OUTCOMES AND FUTURE WORK

5.1. Summary and Outcomes

In this thesis, Pickering emulsion production in baffled stirred tanks was studied. Concentrated oil in water Pickering emulsions with silicon oil as the dispersed phase, water as the continuous phase and hydrophilic glass beads as the stabilizing particle were produced. The physicochemical properties and coverage potential of the system was kept constant by keeping the particle type and concentration constant. The oil type, viscosity and concentration was also kept constant. The effect of hydrodynamics on producing the emulsions was then investigated. The resulting emulsion droplet sizes were measured with a Malvern Mastersizer using a laser diffraction technique.

Two impellers were used at two different sizes to generate different flow patterns: the Rushton turbine for radial flow pattern and the Pitched Blade Turbine (PBT) for mixed flow pattern. The RT impeller was characterized with a better droplet breakup and particle adsorption mechanism, higher shear generation capacity and a higher power number than the PBT impeller. The PBT impeller was characterized with a higher pumping capacity than the RT impeller. The T/2 impellers had a larger shear zone and smaller coalescence zone than the T/3 impellers. The T/3 impellers required higher impeller speeds than the T/2 impellers.

Parameters such as the tip speed, power per mass, Reynolds number and Weber number were used to investigate the effect of hydrodynamics on the droplet sizes produced. The energy dissipated around the impeller zone and the size of the impeller high shear zone (breakup zone) were found to be critical to the droplet size distributions of the emulsions. Higher energy dissipated and larger impeller high
shear zone produced smaller droplets. For different parameters, different impellers can be preferred. At the same tip speeds, impellers with higher power numbers and dispersion geometries should be preferred. At the same power per mass, impellers with larger diameters and better dispersion geometries should be preferred. At the same Reynolds number, there is a dependency on impeller speed. So, the impeller with higher impeller speed and better dispersion geometry should be preferred. The weber number results showed that size of the breakup zone can be more controlling than the energy dissipated by the impeller. The T/2 RT impeller was found to be the most effective impeller; having both high energy dissipation and larger breakup zone. Its effective dispersion geometry also allowed for it to produce the smallest droplets. The T/3 PBT impeller was found to be the least effective impeller as a result of its poor circulation. It also had low energy dissipation and larger coalescence zone compared to the other impellers.

The effect of the change of impeller speed on the emulsion droplet sizes was also investigated for all the impellers. It was investigated in consideration of the suspension of particles, adsorption of particles onto the droplet interface, droplet breakup and droplet coalescence. Mixing time experiments corroborated the results in terms of residence time of the droplets in zones of the tank. For impellers with adequate flow, it was found that increasing the emulsification speed produced smaller droplets and decreasing the emulsification speed produced bigger droplets. A speed hysteresis was observed and the droplets returned to a specific size range after the speed was decreased to the speed it was before.

5.2. Future work

The study in this thesis presents insight into the production of Pickering emulsions in baffled stirred tank. The mechanism of Pickering emulsion droplet formation was observed for two fundamental impeller types. Several topics arise which can be studied to improve on this work and provide more information on the Pickering emulsion production system. The following can be pursued in future studies:
• It was concluded that impellers with greater shear generation, higher power number (energy dissipation) and more effective breakup mechanisms are more favorable for the production of the emulsions. Impellers with higher shear than the Rushton turbine can be designed and implemented to produce the emulsion.

• This study suggests that power per mass is the ideal hydrodynamic parameter to study for emulsion production. Scale-up studies can be done to confirm the results in larger stirred tanks.

• The effect of different types of particles at different (ideally smaller) sizes can be investigated at the same hydrodynamic conditions. Perfectly adsorbing particles with contact angles close to 90º can also be tested. Different oil with varying viscosities can also be studied. The results can be compared with this work.

• The effect of long term mixing: mixing for more than a day can be investigated. There is a possibility that ‘overprocessing’ can occur and the emulsions become destabilized.

• Different stirred tank configurations can be investigated. The off-bottom clearance, baffle width, liquid height/tank diameter ratio can be changed.
REFERENCES


APPENDICES

A. Mixing time video analysis code

% Author: Usman Kayode Abdulrasaq
% For Mixing time Experiment of Msc Thesis,
% Chemical Engineering Department, Middle East Technical University

clc
clear all

%%% Threshold calculations %%%%%
frame1 = imread(x1); % Read first image
red1 = frame1(:,:,1); % Red channel
green1 = frame1(:,:,2); % Green channel
blue1 = frame1(:,:,3); % Blue channel
frameLast = imread(x2);  \%Read last image
redLast = frameLast(:,:,1); \% Red channel
greenLast = frameLast(:,:,2); \% Green channel
blueLast = frameLast(:,:,3); \% Blue channel

%%%Threshold Calculation%%%%%%%
X = 0.5; \% For Bromocresol Purple
thresh_g = green1 + X*(greenLast-green1); \%GREEN
thresh_b = blue1 + X*(blueLast-blue1); \%BLUE
thresh_r = red1 + X*(redLast-red1); \%RED

mixedg = zeros(size(frame1)); \%Pre-allocated for mixed green array
mixedr = zeros(size(frame1)); \%Pre-allocated for mixed red array
mixedb = zeros(size(frame1)); \%Pre-allocated for mixed blue array

Mg = zeros(length(theFiles),1); \%Pre-allocated for mixed green pixels array
Mr = zeros(length(theFiles),1); \%Pre-allocated for mixed red pixels array
Mb = zeros(length(theFiles),1); \%Pre-allocated for mixed blue pixels array
t = zeros(length(theFiles),1); \%Pre-allocated for time array

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%% Loading and re-reading of images
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

for k = 1 : length(theFiles)
    baseFileName = theFiles(k).name;
    fullfile(myFolder, baseFileName);
    fprintf(1, 'Now reading %s
', fullFileName);
    frame = imread(fullFileName); \% Read the files
    red = frame(:,:,1); \% Red channel
    green = frame(:,:,2); \% Green channel
    blue = frame(:,:,3); \% Blue channel

    figure(1)
    imshow(frame) \%\%\%Show the images
    imshow(green) \%\%\%Show the green component images
    drawnow; \% Force display to update immediately.

    [m,n] = size(green);
    N = m*n; \% total number of frames
    for i =1:m
        for j = 1:n

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if green(i,j) > thresh_g(i,j)  \% green component
    mixedg(i,j) = 1;
else mixedg(i,j)=0;
end

if red(i,j) > thresh_r(i,j)  \% red component
    mixedr(i,j) = 1;
else mixedr(i,j)=0;
end

if blue(i,j) > thresh_b(i,j)  \% blue component
    mixedb(i,j) = 1;
else mixedb(i,j)=0;
end

N_mixedg =nnz(mixedg);
Mg(k) = N_mixedg/N;

N_mixedr =nnz(mixedr);
Mr(k) = N_mixedr/N;

N_mixedb =nnz(mixedb);
Mb(k) = N_mixedb/N;

t(k)= 0.04*k;  \%convert to seconds because frames are each 0.04 sec
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%
%%%%%%%% Post processing %%%%%%%
figure(2)
plot(t,Mg,'g') \%Plot green component mixing curve
hold on
% plot(Mb,'b') \%Plot blue component mixing curve
% plot(Mr,'r') \%Plot red component mixing curve

title('Mixedness vs Time')
xlabel('Time(s)') \% x-axis label
ylabel('Mixedness') \% y-axis label
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%