IJCPE
Iraqi Journal of Chemical and Petroleum Engineering

Iraqi Journal of Chemical and Petroleum Engineering
Vol.18 No.1 (March 2017) 121 - 128
ISSN: 1997-4884

University of Baghdad
College of Engineering

Effect of Nanoparticles and Surfactant on Phase Inversion of Two Phases

Nada M. Farhan
Material Engineering Department, University of Technology, Iraq

Abstract

In the present study, a pressure drop technique was used to identify the phase inversion point of oil-in-water to water-in-oil flows through a horizontal pipe and to study the effect of additives (nanoparticles, cationic surfactant and blend nanoparticles-surfactant) on the critical dispersed volume fraction (phase inversion point). The measurements were carried for mixture velocity ranges from 0.8 m/sec to 2.3 m/sec. The results showed that at low mixture velocity 0.8 and 1 m/sec there is no effect of additives and velocity on phase inversion point, while at high mixture velocities the phase inversion point for nanoparticles and blend (nanoparticles/surfactant) systems was delayed (postponed) to a higher value of the dispersed phase volume fraction (oil volume fraction) compared to the system of surfactant where the phase inversion point was occurred at low dispersion phase volume fraction.

For all systems the desperation volume fraction at the point of inversion decreases with increasing mixture velocity.

Indeed, the results showed that surfactant was more effective on phase inversion point than solid nanoparticles.

Key words: Phase inversion, surfactant, nanoparticles, oil-water flow, and pressure drop.

Introduction

The flow of two immiscible liquids (oil-water) two phase flow through a horizontal pipe appears in many industries such as pharmaceuticals, food and especially in crude oil production.

Most of the flow pattern of two immiscible liquids (oil-water) has been observed are dispersed flow where one liquid can be the continuous phase and the other one is dispersed as drops in the continuous phase. The phenomenon of phase inversion occurs when the disperse phase volume fraction increased gradually until it becomes the continuous phase and the originally continuous phase becomes the disperse phase. The critical volume fraction of the dispersed phase where inversion occurs is known as the phase inversion point.

Predicting the phase inversion point has become very important for industries, in designing long distance of transport pipelines of crude oil and in the selection of operating conditions, pumps, downstream separation facilities. Its impotence is due to the fact that at a phase inversion point there is a significant increase in the appearance viscosity of the oil-water mixture leading to increase in the pressure gradient.

The effect of additives such as surfactants (interfacial tension) and solid nanoparticles on phase inversion carried out in batch processes and stirred vessels has been investigated for many years. Selker and Sleicher, [1] suggested that the type of dispersion cannot affected by interfacial tension; Yeh et. al. [2] found that interfacial tension will cause inversion phase at equal volumes of the two liquids; Clarke and Sawistowski, [3] as well as Norato and Tsouris [4] concluded that the phase inversion is more difficult to occur at interfacial tension decreasing: Binks and Lumsdon [5] studied the effect of silica particle concentration, type of oil and oil-water ratio on phase inversion and emulsion stability. Binks and Whitby [6] found that the coalescence of droplets decreases as the particle concentration is increased, due to a decrease in the average drop diameter. Binks et al. [7] found that water in oil emulsion stabilized by using hydrophobic particles and oil in water emulsions stabilized only by using hydrophilic particles in agitator vessel. Varun Malhotra [8] studied the effects of pure stabilizers (either silica nanoparticles or surfactant) and mixed stabilizers (combined silica nanoparticles and surfactant) on phase inversion of water in oil to oil in water in stirred vessels.

A few investigators studied the effect of additives (nanoparticles, surfactant) on phase inversion of two phases (oil-water) flow through pipe such as Salager et al., [9] who studied the phase inversion in the pipes, he found that the composition of the mixture at which the dispersion inverts is changing with surfactant; Piela et al., [10] studied experimentally the influence of the additives of a surfactant and salt on the phase inversion point for water-oil flow through a horizontal pipe. The results showed that, the addition of a surfactant caused a little change in the phase inversion point, but the influence of salt was negligible; Ngana et al., [11] studied the effect of reducing interfacial tension on the phase inversion process by adding a small amount of glycerol in the water phase flow during horizontal pipe. It was found that reducing the interfacial tension causes an increase in the oil volume fraction to complete the inversion process.

Many mechanisms are suggested for predicting the phase inversion, one of the most mechanisms used is the opposite processes of break-up and coalescence of drops (Nienow et al., [12]). Phase inversion occurs when the rate of coalescence for dispersed phase exceeds the rate of break up which leads to increasing in the effective viscosity of the mixture.

(Yeo et al., [13]; Brauner and Ullmann, [14]) concluded that phase inversion occurs at the point where the interfacial energy of oil in water dispersion equal to the interfacial energy of water in oil dispersion.

Another mechanism for explaining phase inversion occurs is a multiple dispersion when the small droplets of continuous phase trapped into the dispersed phase drops, which leads to increase the size of dispersed phase drops and becomes more capability to coalescence (Groeneweg et al., [15] and Bouchama et al., [16])

In this work the effect of additives (nanoparticles, surfactant and mixed surfactant-nanoparticles), on phase inversion point for two phase oil-water flow through a horizontal pipe is investigated under several mixture velocities.

Experimental Work

The schematic diagram of the experimental setup is shown in Figure 1. It consists of an acrylic horizontal pipe with an inner pipe diameter 12.7 mm (to get fully developed dispersion flow) and 6 m in length as a test section, pumps and pressure gauge.

All experiments were conducted using two immiscible liquids tap water, which was used as an aqueous solution (density 998.2 kg/m3, viscosity at 1.002 Cp and Surface tension 72.75 mN/m) and kerosene (density 828 kg/m3, viscosity at 5.5 cp, Surface tension 27.5 mN/m) at room temperature (25 °C) and atmospheric outlet pressure (1bar).

The experiment started by pumping water and white oil from their respective storage tanks (tank 1 and 2) by means of pump 1 and 2 (see Figure 1) into the test section via a T-junction, to ensure minimum mixing of the two liquids at the inlet point .The flow rates of liquids were measured using two flow meters just before entering the test section. After the test section the mixture flows into a separator tank to separate the oil and water by gravity. Water and oil were led by pumps (3 and 4) from the bottom and middle of the separator tank in to the storage tank (tank 1 and 2). Pressure drops were measured simultaneously for each experiment at six different locations over a distance of 1 m from the pipe inlet.

The experimental tests had been conducted under different mixture velocities 0.8, 1, 1.9 and 2.3 m/s. The experiments started with the flow of water phase for few seconds through the horizontal pipe to ensure that the pipe wall was wetted by the water. After that, the dispersed oil fraction gradually increased by increasing the oil flow rate and decreasing water flow rate to keep the mixture velocity constant, this continued until inversion was observed and beyond up to single phase of oil flow.

Each experiment run was repeated three times to confirm the results. And the averaged results were reported here.

In order to study the effect of additives on phase inversion, two types of additives were used titanium nanoparticles at 100 ppm (surface tension 61 mN/m), hexadecltrimethyl ammonium bromide (CTAB) at 100 ppm (surface tension 39 mN/m) and blend of CTAB/titanium nanoparticles at 200ppm (surface tension 48 mN/m). The physical properties of the titanium nanoparticles are tabulated in Table 1.

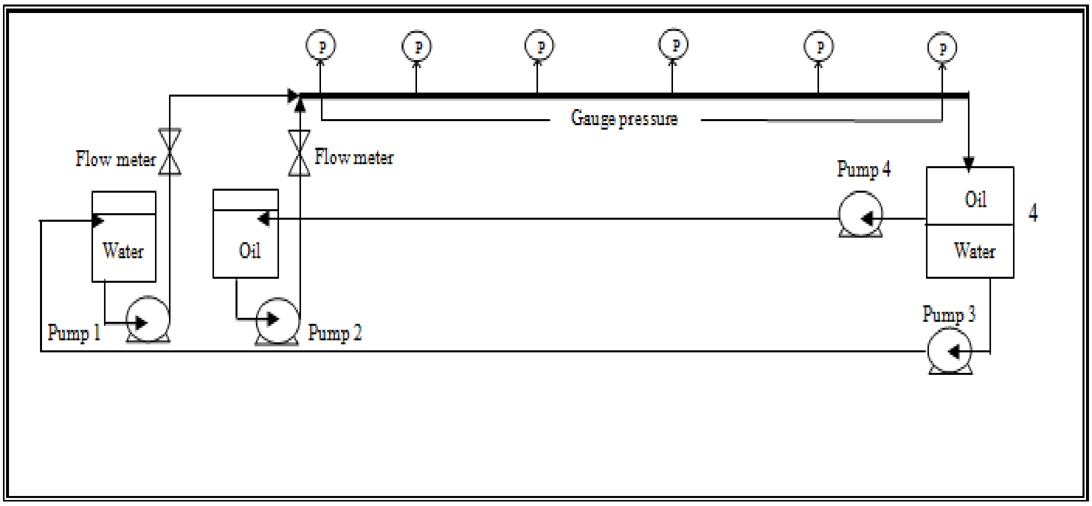


Fig. 1: The schematic diagram

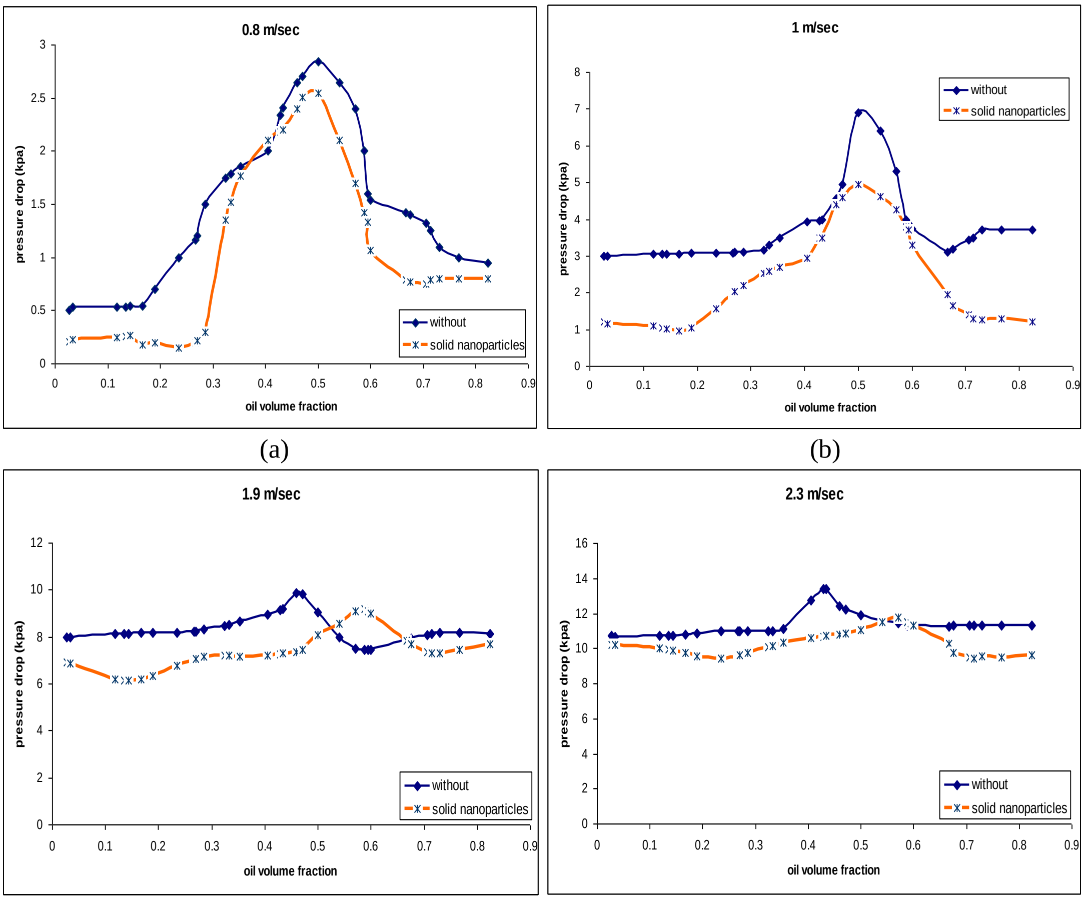
Table 1: Physical properties of titanium nanoparticles

	Titanium nanoparticles
Density (kg/m^3)	423
Surface tension (mN/m)	61
Average Nanoparticle Size	50 nm
Specific Surface Area	160 m^2/g
Color	White

Results and Discussion

1. Effect of Solid Nanoparicles

Figure 2 shows the pressure drop as a function of the oil fraction for a wide range of mixture velocities (0.8, 1, 1.9 and 2.3 m/s) with Reynolds number ranged from 6903 to 22158. The results observed that at low mixture velocities 0.8 and 1 m/sec the influence of the solid nanoparticles on the phase inversion point is negligible. At high values of mixture velocity 1.9 and 2.3 m/sec the influence of the solid nanoparticles on the phase inversion point is significant. The phase inversion shifted forward (0.588 and 0.57 oil fraction) with respect to the inversion point for the case without any additives (0.45 and 0.43) respectively.



(a) (b)

(c) (d)

Fig. 2: Effect of solid nanoparticles on phase inversion for different mixture velocity [(a) 0.8, (b) 1, (c) 1.9 and (d) 2.3] m/sec

This can be explained by the nanoparticle physical properties and its type. It is well known that nanoparticles classified into two groups according to the hydrophobicity of particles; low hydrophobicity (hydrophilic nanoparticles) the nanopraticles are preferentially wetted by the water phase (nanoparticles are initially dispersed in aqueous solution and preferred aqueous solution to be the continuous phase), and high hydrophobicity (hydrophobic nanoparticles) the nanoparticles are preferentially wetted by the oil phase (nanoparticles are initially dispersed in oil phase and preferred oil to be the continuous phase).

Titanium nanoparticle is one of the hydrophilic nanoparticle types. Its addition leads to prefer water to be the continuous phase, thereby improving water wetting of particle surface which favors stability of oil dispersion phase in water continuous phase and reducing their potential of coalescence due to the decreasing in the average drop diameter. This required higher dispersed phase fraction (oil fraction) to occur inversion.

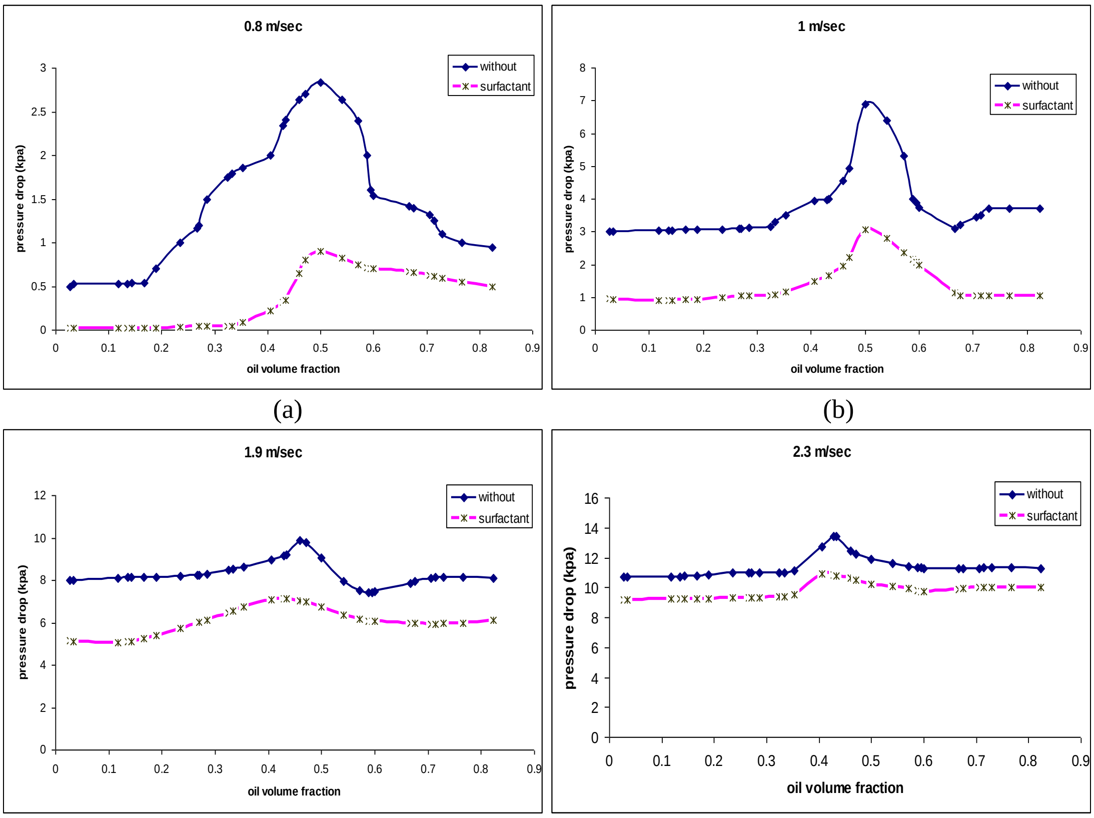
2. Effect of Surfactant

The presence of surfactant can have a significant influence on the inversion process; they tend to favor one type of dispersion over the other. It is well known that surfactant posses an equal ratio between the polar and nonpolar portions. When placed in an oil-water system, the polar groups (hydrophilic head) are attached to water, while non polar groups (hydrophobic tail) are oriented to the oil. The mechanism of surfactant depends mainly on lowering the interfacial tension between two liquid oil and water phase. The interfacial tension is lowered due to the adsorption of surfactant molecules at the oil-water interface. Indeed, some of them keep the drops of oil in water by charging their surfaces that reduce the physical contact between drops and allowing easier spreading of one liquid on the other.

Figure 3 shows that at low mixture velocities 0.8 and 1 m/sec the influence of the CTAB surfactant on the phase inversion point is negligible but at high values of mixture velocity 1.9 and 2.3 m/sec the addition of CTAB to the continuous phase (water) shows different behavior in which the phase inversion shifted downward (0.42 and 0.4 oil fraction) with respect to the inversion point for the case without the surfactant addition (0.45 and 0.43 oil fraction) respectively. This can be attributed to the physical nature of surfactent. If it is inonic (hydrophopic head), ctaionic (hydrophilic head) or non ionic type. CTAB is one of the cationic surfactant types (highly hydrophobic surfactant), its positive charge allowed it to adsorb on the interface where it acts to lower the interfacial tension and to elicit Marangoni stresses. This effect slows down the drainage of the continuous phase film between two opposing drops, which is an essential step to increase the coalescence of oil drops leading to decrease the volume fraction of dispersed phase will thus be needed to occur inversion.

3. Effect of Blend Additives (Solid Nanoparticles-Surfactant)

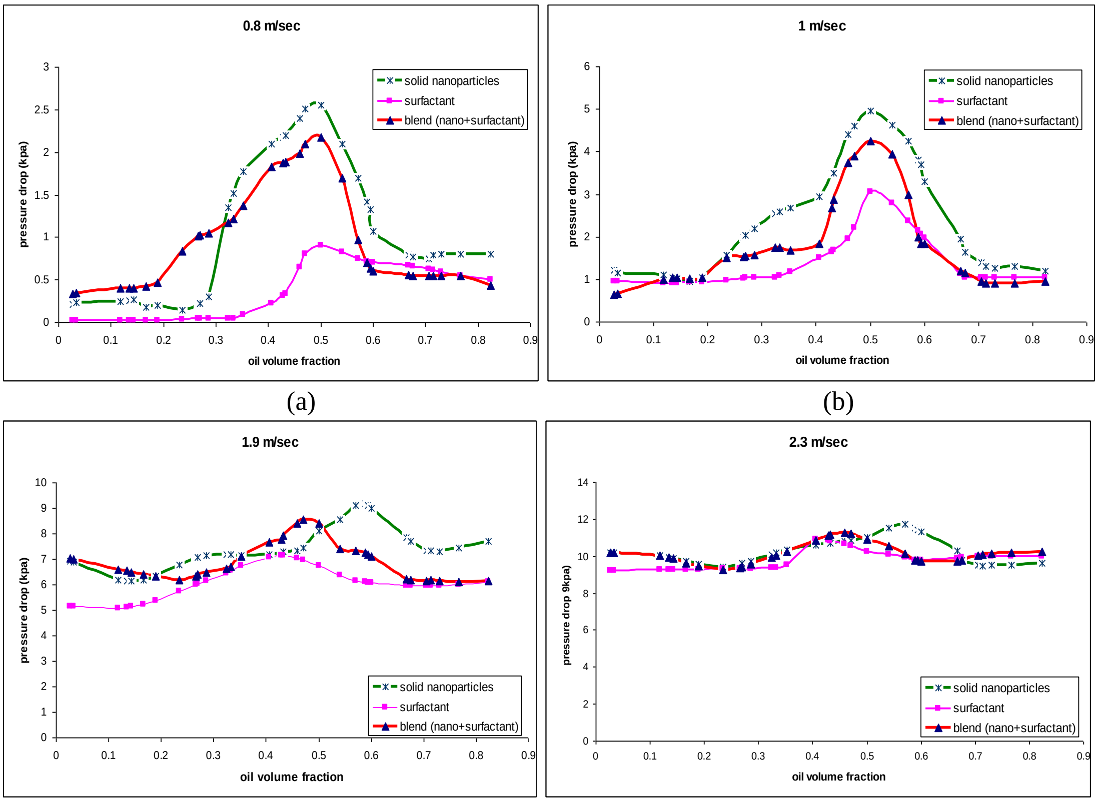
The effect of blend additives (100 ppm titanium nanoparticles and 100 ppm CTAB at total concentration 200 ppm) on phase inversion is shown in Figure 4. The figure shows that the oil volume fraction at which inversion occurs nearly constant at low mixture velocities 0.8 and 1 m/s. At high mixture velocity 1.9 and 2.3 m/sec the inversion point occurred at (0.47 and 0.459 oil fraction) with respect to inversion point of the surfactant system (0.42 and 0.4 oil fraction) and inversion point of the nanopraticles system (0.588 and 0.57 oil fraction). This clearly demonstrates that the surfactant is much more effective than nanoparticles in phase inversion process.



(a) (b)

(c) (d)

Fig. 3: Effect of surfactant on phase inversion for different mixture velocity [(a) 0.8, (b) 1, (c) 1.9 and (d) 2.3) m/sec



(a) (b)

(c) (d)

Fig. 4: Effect of blend additives (solid nanoparticles + surfactant) mixture on phase inversion for different mixture velocity [(a) 0.8, (b) 1, (c) 1.9 and (d) 2.3] m/sec

On the other hand, Figures 2, 3 and 4 show that there is no influence of additives on phase inversion point at low mixture velocities (there is no changing in phase inversion point).

At high mixture velocities 1.9 and 2.3 m/s, the oil fraction at which phase inversion occurred lowered to (0.45 and 0.43) than that without any additives, (0.42 and 0.4) for surfactant addition, (0.588 and 0.57) for titanium nanoparticles addition and (0.47 and 0.459) for mixing surfactant / nanoparticles addition. This can be attributed to the fact that the turbulence in pipe flow dominates the mixing between the two liquids leading to high interaction between them.

Indeed, Figures 2-4 show that for all system the pressure drop increases with increasing mixture velocity. Due to the strong interaction between oil-water two phase flow at high mixture velocities. Also, this Figures 2-4 show that the pressure drop increases at inversion point for all systems. This attribute to the increase in the effective viscosity of two liquids at this point. The peak in pressure drop became sharper and bigger with increasing mixture velocity for all systems, due to the growth of the effective viscosity increasing with the increase of mixture velocity; (Ioannou et al., [17]; Piela et al., [18]).

Conclusions

The experiments observed that the presence of either surfactant or solid nanoparticles and (surfactant / nanoparticles) mixture have a significant influence on phase inversion point at high mixture velocities 1.9-2.3 m/sec, the dispersed oil volume fraction at inversion point (0.588-0.57) for nanoparticles and (0.47-0.459) (nanoparticles/surfactant) mixture systems are higher than (0.42-0.4) for surfactant system. In the (surfactant/nanoparticles) mixture the surfactant has a more effect on phase inversion point rather than solid nanoparticles. At low mixture velocity the phase inversion point was unaffected by increasing mixture velocity neither by additives.

References

1. Selker, A., Sleicher, Jr., C.A., 1965. Factors affecting which phase will disperse when immiscible liquids are stirred together. Can. J. Chem. Eng. 43 (6), 298–301.
2. Yeh, G., Haynie, F.H., Jr. and Moses, R.E., 1964, Phase–volume relationship at the point of phase inversion in liquid dispersions. AIChE J, 102: 260.
3. Clarke, S.I., Sawistowski, H., 1978. Phase inversion of stirred liquid/liquid dispersions under mass transfer conditions. Trans. IChemE 56, 50–55.
4. Norato, M.A., Tsouris, C., Tavlarides, L.L., 1998. Phase inversion studies in liquid–liquid dispersions. Can. J. Chem. Eng. 76, 486–494.
5. Binks, B.P. and Lumsdon, S.O., (2000a). Catastrophic Phase Inversion of Water-in-oil Emulsions stabilized by Hydrophobic Silica. Langmuir, 16, 2539-2547.
6. Binks, B.P. and Whitby, C.P., (2003). Silica Particle-Stabilized Emulsions of Silicone Oil and Water: Aspects of Emulsification. Langmuir, 20, 1130-1137.
7. Binks, B.P., Philip, J. and Rodrigues, J.A., (2005). Inversion of Silica-Stabilized Emulsions induced by Particle concentration. Langmuir. 21, 3296-3302.
8. Malhotra V., (2009). Effects of Mixed Stabilizers (_anoparticles and Surfactant) on Phase Inversion and Stability of Emulsions. M.Sc. thesis, University of Waterloo, Ontario, Canada.

9. Salager, J.L., Márquez, L., Pèna, A.A., Rondón, M., Silva, F., Tyrode, E., 2000. Current phenomenological know-how and modeling of emulsion inversion. Ind. Eng. Chem. Res. 39, 2665–2676.
10. Piela, K., Djojorahardjo, E., Koper, G.J.M.,and Ooms, G., 2009, Influence of a surfactant or salt on phase inversion in a water–oil pipe flow. chemical engineering research and design, 8 7, 1466–1470.
11. Ngan K. H., Ioannou K., Rhyne L. D., Angeli P., 2011, Effect of glycerol addition on phase inversion in horizontal dispersed oil–water pipe flows. Experimental Thermal and Fluid Science. 35, 628–635.
12. Nienow, A., 2004. Break-up, coalescence and catastrophic phase inversion in turbulent reactors. Adv. Colloid Interface Sci. 108, 95–103.
13. Yeo, L.Y., Matar, O.K. and Perez de Ortiz, E.S., 2002, A simple predictive tool for modelling phase inversion in liquid–liquid.
14. Brauner, N., Ullmann, A., 2002. Modelling of phase inversion phenomenon in two-phase pipe flows. Int. J. Multiphase Flow 28, 1177–1204.
15. Groeneweg, F., Agterof, W., Jaeger, P., Janssen, J., Wieringa, J., Klahn, J., 1998. On the mechanism of the inversion of emulsions. Trans IChemE A 76.
16. Bouchama, F., van Aken, G., Autin, A., Koper, G., 2003. On the mechanism of catastrophic phase inversion in emulsions. Colloids Surf. A: Physicochem. Eng. Aspects 231, 11–17.
17. Ioannou, K., Nydal, O.J., Angeli, P., 2005, Phase inversion in dispersed liquid-liquid flows, 29, 331-339.
18. Piela, K., Delfos, R., Ooms, G., Westerweel, J., Oliemans, R.V.A., 2008, On the phase inversion process in an oil–water pipe flow. International journal of multiphase flow, 34, 665–677.