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Developing techno-economically sustainable methodologies for deep desulfurization using hydrodynamic cavitation

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ABSTRACT

The present work, for the first time, describes the efficacy of the cavitation process and compares the cavitation yield for two types of cavitation devices-one employing linear flow for the generation of cavities and other employing vortex flow. The process involves pre-programmed mixing of the organic and aqueous phases, and can be carried out using simple mechanical cavitating devices such as orifice or vortex diode. The process essentially exploits *in situ* generation of oxidising agents such as hydroxyl radicals for oxidative removal of sulfur. The efficiency of the process is strongly dependent on the nature of device apart from the nature of the organic phase. The effects of process parameters and engineering designs were established for three organic solvents (n-octane, toluene, n-octanol) for model sulfur compound-Thiophene. A very high removal to the extent of 95% was demonstrated. The results were also verified using commercial diesel. The cavitation yield is significantly higher for vortex diode compared to the orifice. The process has potential to provide a green approach for desulfurization of fuels or organics without the use of catalyst or external chemicals/reagents apart from newer engineering configurations for effective implementation of hydrodynamic cavitation in industrial practice and also appears to be economically sustainable.

1. Introduction

1.1. Desulfurization

Air pollution due to burning of fossil fuels is a major challenge and removal of sulfur from transportation fuels is an essential operation in petroleum refineries for reduced pollution due to SOx emission. The vehicular pollution in many major cities in many parts of the world has reached alarming proportion, forcing Governments worldwide to continuously enforce increasingly stricter norms for sulfur content in fuels for improved environmental sustainability. Euro-VI norms demand sulfur concentration in diesel and petrol to be less than 10 ppm [1], compared to earlier norms of 350 and 500 ppm in diesel and gasoline, subsequently lowered to the level of 15 ppm and 30 ppm in diesel and gasoline respectively [2–4]. Increased focus on newer developments such as fuel cell applications also demands more stringent limits on the sulfur levels (less than 1 ppm) to avoid poisoning of the catalyst. Biodiesel also can contain appreciable amounts of sulfur that requires processing in terms of sulfur reduction for sustainable applications [5].

The existing refinery operations have limitations with respect to satisfactory sulfur removal apart from the economics of the processes pertaining to the sulfur removal. There are a number of sulfur compounds in fuels that have varying concentrations and most importantly these vary in their reactivity as far as catalytic desulfurization is concerned demanding severe process conditions in terms of high temperature/pressures or newer catalysts. Conventional hydrodesulfurization (HDS) though suitable for lowering sulfur content up to 350 ppm, requires supplementary processes such as oxidation, adsorption or newer forms of processes that are capable of removing remaining refractory compounds to desired levels [6–8]. In view of the fact that huge volumes of fuels have to be processed techno-economically, there appears to be limited options for replacing the conventional HDS process that employs catalyst such as Co-Mo or Ni-Mo and requires high temperatures of the order of 450 °C, along with high pressures of the order of 20–40 atm. Thus, it is apparent that though the HDS process can meet the new standards with certain modifications such as

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Nomenclature

C	Cost of operation (kWh/kg)
P	Pressure (bar; N/m^2)
R	Amount of sulfur removed (mg)
Rs.	Indian rupees
Q	Flow rate (LPH; m^3/s)
T	Temperature (K)
t	Time (s)
v	Volume (m^3)
V	Total volume (m^3)
Y	Cavitational yield (mg/J)
ΔP	Pressure drop (bar; N/m^2)
σ	Efficiency of pump

increased (~3-fold) catalyst volume/reactor size and increased cost of operation, a more suitable practice would be to employ greener routes that can be integrated into the existing plant for better techno-economic feasibility and sustainability. The alternative can be in the form of adsorptive desulfurization using conventional adsorbents to π-complexation adsorbents [4,9–14], biodesulfurization [6,15] and oxidative desulfurization [16,17]. Recently, oxidation processes in different forms have been increasingly discussed for desulfurization of fuels which also include processes that combine oxidation and extraction (Extractive and catalytic oxidative desulfurization or ECOD). In these, more thrust is placed on developing/evaluating various catalysts for oxidation and suitable extractants for removing oxidation products [18–20]. Cavitation, which is also one form of advanced oxidation process, has also been discussed largely using catalysts for desulfurization. Commonly, ultrasound assisted oxidative desulfurization is reported in presence of various catalysts for different substrates [21–25], while hydrodynamic cavitation is rarely used, that too using catalyst such as hydrogen peroxide [26]. Different fuel fractions such as gasoline, jet fuel, and diesel have different compounds from lower end compounds of sulphides, disulfides, mercaptans to refractory compounds such as thiophene, benzothiophene, dibenzothiophene and such alkylated derivatives of thiophene. Different desulfurization processes have a varying degree of success in removal of these varied forms of sulfur compounds and face severe challenges in the satisfactory and efficient removal of refractory sulfur compounds. Thiophene is one of the most difficult and refractory organic sulfur compound as far as oxidative desulfurization is concerned and hence its effective removal is crucial [27–29].

Recently, a non-catalytic process for deep desulfurization of fuels employing hydrodynamic cavitation with vortex diode for generating vortex flow for cavitation was reported [27] with a very high sulfur removal for thiophene. It is instructive to study, the impact of the engineering designs of cavitating devices and also evaluate techno-economic sustainability. In this work, the main objective is to report extensive studies on hydrodynamic cavitation for deep desulfurization of fuels and organics without employing any catalyst and under mild operating conditions, but using linear flow for cavitation, orifice as a cavitating device, compare the performance with that of vortex diode and finally evaluate economic feasibility. Thiophene was chosen as a model sulfur compound mainly due to the limitation of conventional oxidation processes in its removal [30] and also for ease of comparison of the different processes in this regard. Cavitational yields have been discussed in different forms of cavitation apart from establishing the applicability of cavitation method based on hydrodynamic cavitation for sulfur removal, especially by obtaining insight into the sulfur removal behaviour not just for different cavitating devices, but also for

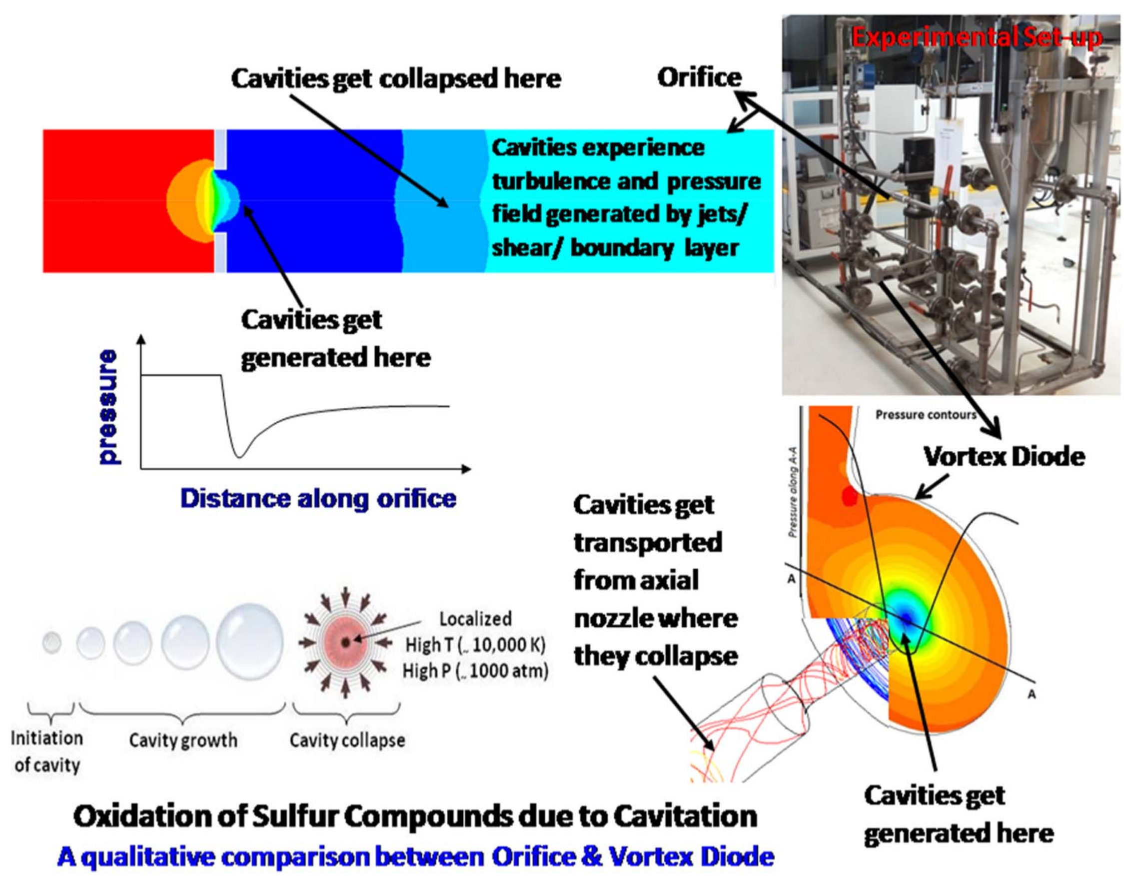

Fig. 1. Schematic representation of cavitation process in Orifice and Vortex Diode.