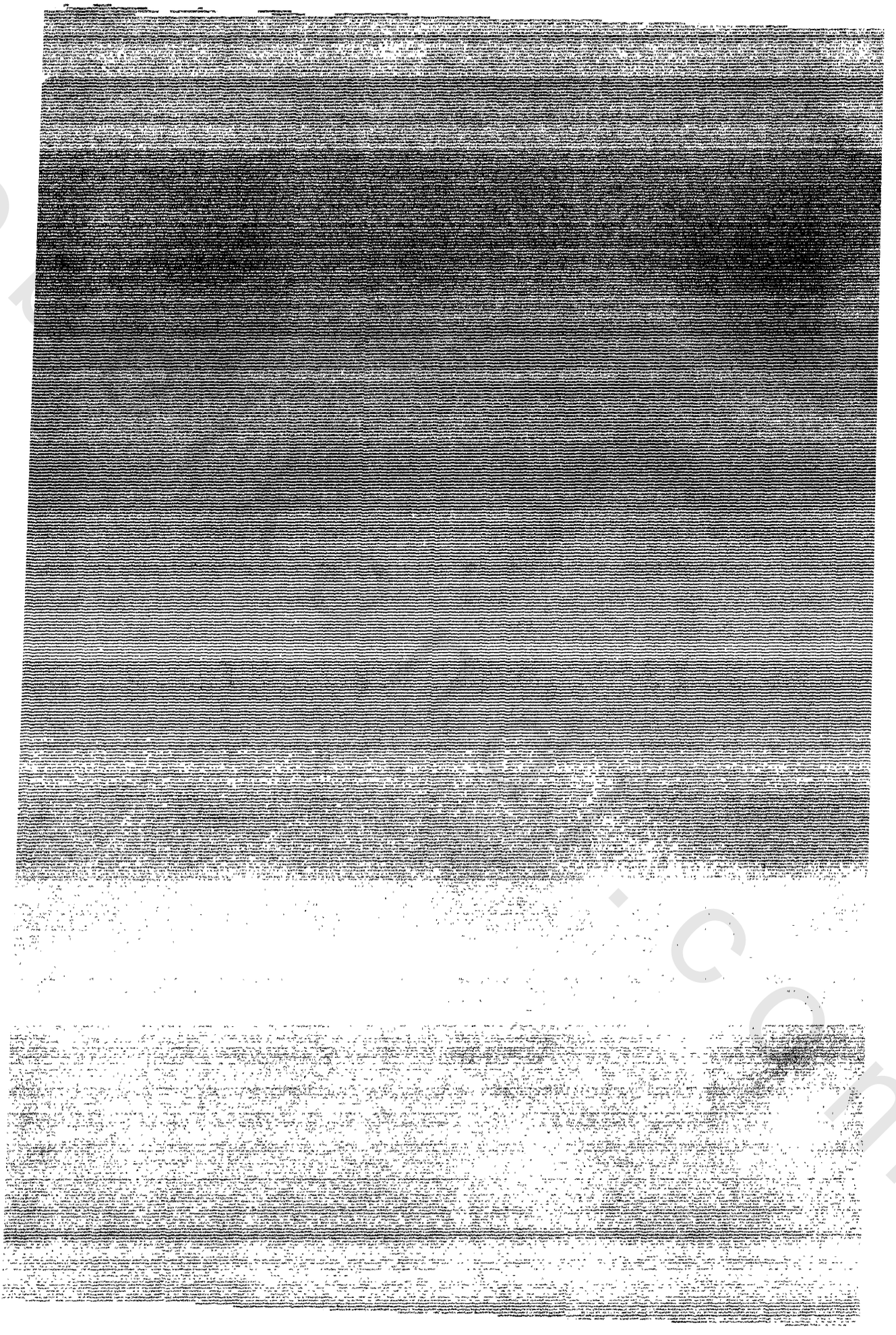
Chapter 1 Introduction



INTRODUCTION

It is well known that hydrotreatment is used in the refining industry to remove contaminants such as sulfur (HDS) hydrodesulfurization, nitrogen (HDN) hydrodenitrogenation, metals (HDM) hydrodemetalization, mainly because of technical and environmental reasons **[Jiménez et al., 2007].**

Hydroprocessing removes various contaminants from the crude oil and results in the finished oil products having improved odor, color and stability characteristics. In addition to reducing the amount of heavy residue, hydroprocessing also increases the volume of more valuable oil fractions produced **[Eijsbouts et al., 2008].**

In recent years, sulfur reduction from light gas oil using catalytic hydrodesulfurization (HDS) is a routine operation in petroleum refining processes because the environmental regulations have become more and more strict, limiting the amount of sulfur permitted in fuels and gas oil to < 0.01 wt%.

The removal of sulfur-containing compounds such as thiophenes, mercaptans, dibenzothiophene and especially its alkylsubstituted derivates, is necessary in order to minimize the polluting effects of sulfur-containing gases such as SO_2 that may be released into the atmosphere **[Ramirez and Minero, 2008] [Frizi et al., 2008].**

An improved HDS catalyst and/or processes, which achieve deep HDS at low temperatures and hydrogen pressures, are required to satisfy economic considerations. In the refining industry, γ- alumina supported molybdenum or tungsten-based catalysts promoted with cobalt or nickel have been widely used for the HDS of sulfur compounds **[Castellón et al., 2008].**

The life cycle of a hydroprocessing catalyst starts with the initial production of fresh oxidic catalyst, which is presulfided prior to being used in the refinery process. During its use, the catalyst deactivates and, as soon as the catalyst does not meet the performance targets within the limits of the reactor operating condition, the reactor is shut down. Depending on the degree and nature of catalyst contamination, the catalyst can be either directly regenerated, undergo an additional reactivation / rejuvenation treatment or has to be recycled / disposed of **[Eijsbouts et al., 2008].**

One of the major problems related to the operation of heterogeneous catalysis is the catalyst loss of activity with time- on –stream, i.e. "deactivation" **[Forzatti and Lietti, 1999].** Deactivation of the catalyst can occur for several reasons. For example, accumulation of nickel and vanadium deposits, their plugging some of the small pores in the catalyst.

Catalyst deactivation is a phenomenon of great economic impact on many industrial processes. One of the main causes of deactivation is coke formation, which consists in the deposition of significant amounts of carbonaceous residues onto the catalyst surface. These deposits reduce the activity of the catalyst because they block the active sites and distort

the porous structure **[Reis, 2005] [Froment, 2001] [Glasson et al., 2002].** It is well established that coke formation depends on the operating conditions, the type of catalyst and the reactor feed composition **[Martin et al., 2005].**

The study of catalyst deactivation during hydroprocessing of heavy oil fractions is one of the most important aspects to improve the catalytic performance in petroleum refining processes **[Ancheyta et al., 2003] [Furimsky and Massoth, 1999] [Maity et al., 2007] [Vogelar et al., 2006].**

Cokes formed very rapidly during the first hours of time - on stream, and deactivation of catalyst by this material appears to rapidly reach a pseudo steady state level **[Hauser et al., 2005] [Matsushita et al., 2004] [Morel et al., 1997].**

In most refineries, a major portion of the spent catalyst waste comes from the residue hydrotreaing and hydroprocessing units. This is because the catalysts used in these processes deactivate rapidly by coke and metal (V and Ni) deposits, and have a short life **[Al-Dalama and Stanislaus, 2006].**

Catalysts deactivation is caused by: metal deposition on active catalytic surface which is irreversible and whose rate depends on the metal level in the feed; the carbonaceous material deposition and precipitation on the external as well as internal structure of catalyst, pore constriction and blockage, characterized by a very strong loss in activity **[Tailleur and Capriodi, 2005].**

Metals, mainly vanadium build up until the pore becomes pore mouth plugged. With a low- metals feed- stock, there is an initial activity loss as coke is deposited on the catalyst. This is followed by a more gradual loss in activity as the metals deposited. However, with a high metals feed stock, there is a more

rapid and severe deactivation after the initial coke deposition **[Furimsky, 1998] [Beaton and Bertolacini, 1991] [Rana et al., 2007] [Ancheta et al., 2005] [Takatsuka and Hori, 1998],** while metals in the feed (mainly V and Ni) are converted to their sulfides, which deposit within the pores and irreversibly deactivate.

The oxidative regeneration procedure removes the coke, whilst the sulfides of Mo/W and Ni/Co are transformed back into oxides. The regeneration can neither remove the metal deposits nor restore the sintering of Ni/Co and W components of the active phase.

The dispersion and homogeneity of the regenerated catalysts are typically better than in the used catalysts, but worse relative to the fresh ones **[Eijsbouts et al., 2008].**

Regeneration is carried out by burning off the deposits in an oxygen – rich stream. Logically, regenerate composition is related to the necessity of avoiding excessive temperature rises that may damage the catalyst.

The temperature needed for regeneration must be carefully controlled to avoid catalyst sintering **[Delmon and Grange, 1980] [Pierre, 2007] [Christoph and Andreas, 2005].**