Vibrational Spectroscopy 83 (2016) 85–93

Contents lists available at ScienceDirect

Vibrational Spectroscopy

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

Measurement of the hydrogenation level of dibenzyltoluene in an innovative energy storage system

P. Inhetveen*, N.S.A. Alt, E. Schluecker

Institute of Process Machinery and Systems Engineering, Friedrich-Alexander-Universitaet Erlangen-Nuernberg, Cauerstr. 4, 91058 Erlangen, Germany

ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form 20 January 2016
Accepted 21 January 2016
Available online 26 January 2016

Keywords:
In-situ raman spectroscopy
Hydrogen
LOHC
Renewable energy
Energy storage

ABSTRACT

The share of renewable energy in the major advanced economies has increased during the last years in order to cope with the limited stocks of fossil fuels. Since the use of renewable resources goes hand in hand with well-known problems as for example the fluctuating availability, energy storage systems are the methods of choice to deal with this issue. One of the most promising storage technologies consists in using hydrogen which can be stored amongst others by hydrogenation of Liquid Organic Hydrogen Carriers (LOHC). During the catalytic hydrogenation of LOHC double bonds are broken down to single bonds and the hydrogen is bound chemically sTable Since this approach is still in development phase, it is necessary to evaluate this storage technology using known measuring methods. Raman Spectroscopy is a method to measure the change of the level of hydrogenation at the time and place of manufacture due to the change of the number of double bonds. The aim is to develop a method to evaluate this storage facility to depict changes in the process conditions directly. This study represents the groundwork, which is needed to implement Raman Spectroscopy as an in-situ online-measurement system to evaluate the performance level of a novel energy storage system.

1. Introduction

The usage of renewable energy sources for electric power generation has increased significantly during the last years as shown exemplary for some of the major advanced economies in Fig. 1 [1–3].

One of the main challenges in the increasing importance of renewable energy sources, especially solar and wind power, is the fluctuating deployment due to meteorological, seasonal and local impacts (see Fig. 2).

This leads to variations in supply and demand which means there are times of higher production than demand and vice versa. These unsteady availabilities indicate the need of energy storage technologies to cope with this issue. There are several approaches to store electrical energy but hydrogen should be the most promising method compared to other ”green technologies” as indicated in Fig. 3.

As shown in Fig. 3, hydrogen has the highest energy density (after gasoline) and similar power densities compared to other methods. Compressed air energy storage and pumped storage technologies are not considered in this context due to relatively weak response time. The generated hydrogen has to be stored until it is needed again. The commonly used methods to save electrical energy in form of hydrogen are divided in:

a) physically
    i. high-pressure gas containers
    ii. cryogenic liquidized hydrogen
b) Power-to-Gas
    i. in form of methane
    ii. in form of methanol
c) energy carrying substances
    i. solids
    ii. LOHC liquid organic hydrogen carrier
    iii. metal hydrides

One main disadvantage of hydrogen serving as ”green fuel” is its volumetric storage density which makes storage in an efficient and safe manner difficult [4–6].

The most common method of storing H2 is usually under very high pressures (up to 700 bar) or as a liquid ($T < 20Ks$) with providing good but still not optimal volumetric energy densities (1.25kWh/1 at $p = 690$ bar and $T = 288$ K, or 2.36kWh/1 as a liquid [7]). Additionally, there is a lack of infrastructure for distributing the gaseous or liquefied hydrogen, which makes it difficult to make it available like natural gas or electricity without establishing or

---

* Corresponding author.
E-mail address: in@ipat.uni-erlangen.de (P. Inhetveen).

http://dx.doi.org/10.1016/j.vibspec.2016.01.008
0924-2031/

Nomenclature

AH	Asymmetric Huber function
ATQ	Asymmetric truncated equation
DBT	Dibenzyltoluene
IR	Infrared
NMR	Nuclear magnetic resonance
PCA	Principal component analysis
phDBT	Per-hydro-dibenzyltoluene
PLS	Partial least square
SH	Symmetric Huber function
STQ	Symmetric truncated equation
A	Fit parameter
a	polynomial coefficients
$A_{i,j}$	Peak area
$AR_{i,j}$	Peak area ratio
B	Divergence of ratio R and fi
b	Background
$\hat{b}_{PLS}$	Regression coefficient
E	n by m- matrix (residuals)
e	Residual
f_i	Factor
$H_{i,j}$	Peak height
$HR_{i,j}$	Peak height ratio
I_0	Incident laser intensity
I_R	Raman scattered radiation
j	Index for considered peak
LOH	Level of hydrogenation
m	Slope
N	Number of molecules
P	m by A- matrix (loadings)
P_{el}	Electrical power
$\hat{P}_{PLS}$	X-scores
p	Polynomial parameter
Q	Vibrational amplitude
$\hat{q}$	Y-loadings
R	Ratio
R^2	Correlation factor
s	Threshold
SD	Standard deviation
T	Wavenumber Vandermonde matrix
$\hat{T}_{PLS}$	n by A- matrix (scores)
$t_{int,i}$	Integration time
$\dot{V}$	Flow rate
$\hat{W}_{PLS}$	X-loadings
w	Peak width
x	Initial value
x_c	Center of peak
x_p	Measured spectra of a sample
y	N-point spectrum
y_L	linear fitting function
y_0	Fit-Parameter
y_{BG}	BiGauss fit function
y_L	Gauss fit function
$y_{i,j}$	Fit function for level of hydrogenation in terms of considered peak j and integration time i
y_L	Lorentz fit function
$\hat{y}_{p,PLS}$	Predicted level of hydrogenation
ν	Wavenumber;
φ_{AH}	Asymmetric Huber function
φ_{ATQ}	Asymmetric truncated function;
φ_C	General cost function; φ_{SH}symmetric Huber function;
φ_{STQ}	Symmetric truncated function

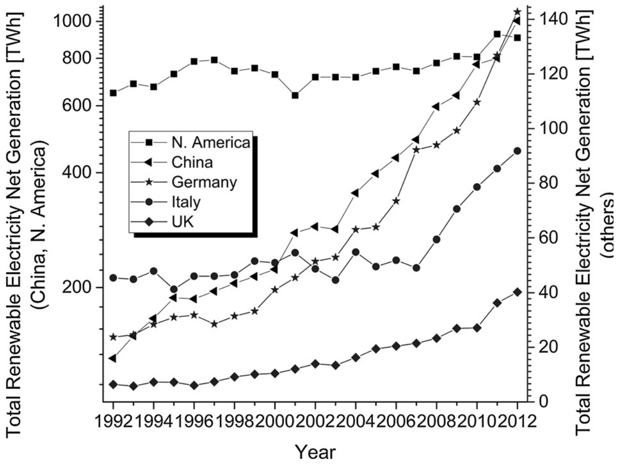

Fig. 1. Electricity Net Generation with renewable resources in general [1].

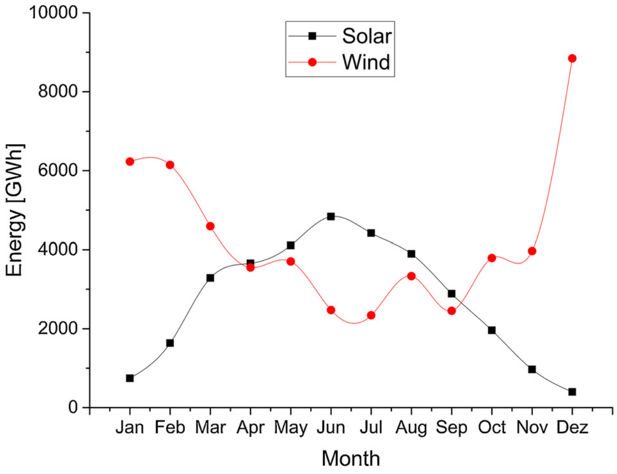

Fig. 2. Annual electrical energy production with solar and wind power in 2014 [2].

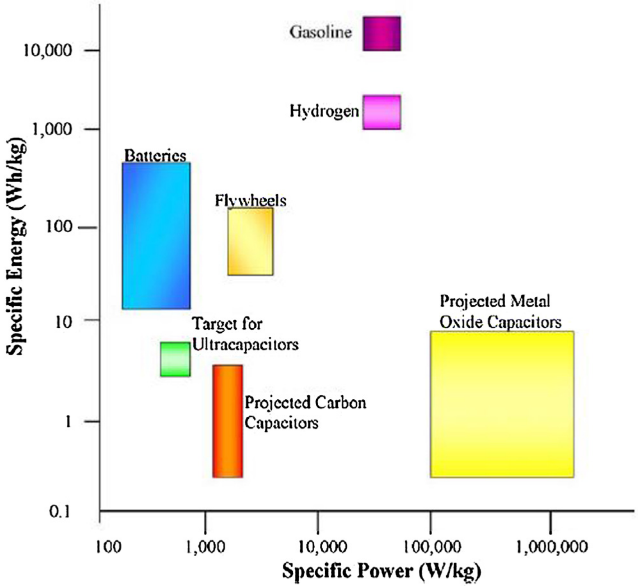

Fig. 3. Comparison of available storage technologies [3].